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## RESISTANCE OF COATED AND UNCOATED IR WINDOWS TO SEAWATER CORROSION

Phase V - Summary

J.D. Stachiw  
S.L. Bertic

1 February 1981

Prepared for  
Naval Electronic Systems Command  
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21. ABSTRACT (Continue on reverse side if necessary and identify by block number) Specimens of germanium, chalcogenide glass, and zinc selenide were submerged in seawater for testing periods up to 4 months and the deterioration of their surface was noted. Some of the specimens tested were coated with single- or multiple-layer antireflection (AR) coatings, while others had protective coatings of various types or were bare. The specimens were subjected (when submerged, out of the water, or both) to several procedures designed to inhibit fouling. Chalcogenide AMTIR-1 (Ge <sub>33</sub> As <sub>12</sub> Se <sub>55</sub> ) glass specimens and germanium coated with AMTIR-1 chalcogenide glass exhibited excellent corrosion resistance. The multilayer durable antireflective coating, Exotic Materials 40100, although not as corrosion-resistant as chalcogenide glass coating, exhibited the best corrosion resistance of all the AR coatings tested in the study. Antireflective, thick carbon coating applied to germanium by		

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Honeywell, Inc, provided good corrosion resistance but still suffered from a larger amount of pinholes than the best multilayer AR coating tested. It had the advantage, however, of excellent hardness and scratch resistance which was significantly superior to any other coating tested in this study.

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## PROBLEM

Thermal imaging systems have many potential uses in the marine environment. Of primary concern to the designer is the selection of window material. These windows must transmit radiation in the desired 8-to-14- $\mu\text{m}$ -wavelength range, meet established structural parameters, and at the same time resist any corrosive action by the marine environment.

## APPROACH

An experimental approach to the problem was taken, which involved the testing of various window materials and coatings for windows. Specifically, specimens of trial materials were tested by exposure to seawater. Antifouling approaches tested included forced seawater circulation, electric resistance current heating, copper ion leaching, and fresh-water rinsing. The specimens fell into five main categories: competitive substrate materials, uncoated; single-layer AR coatings on germanium and zinc selenide; multiple-layer AR coatings on germanium; overcoatings on AR coatings on germanium; and non-AR coatings on bare germanium. The testing took place from March 1977 to November 1980 at NOSC testing facilities.

## RESULTS

The test specimens were wetted by seawater on one face only, and this face was cleaned and dried after removal from the ocean prior to transmittance testing. The findings were formulated on the basis of observations made during the testing. The most promising results are as follows:

1. The specimens of chalcogenide AMTIR-1 glass ( $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ ) showed no signs of corrosion and suffered no loss of transmittance after 4 months' exposure to seawater. The uncoated chalcogenide AMTIR-1 glass had higher transmittance (approximately 70 percent at 10  $\mu\text{m}$ ) than germanium coated with chalcogenide glass on both faces.
2. The germanium specimen coated with the Exotic Materials 40100 multiple-layer durable AR incurred very little damage from corrosion. Less than two dozen pinpoint pits were observed on the 3-inch-diameter specimen after 4 months' exposure to seawater, and there was no significant decrease in transmittance over the 8-to-14- $\mu\text{m}$  wavelength range. The transmittance of a germanium specimen coated on both faces with multilayer 40100 coating was approximately 97 percent at 10- $\mu\text{m}$  wavelength.
3. Of the germanium specimens supplied by Honeywell with carbon coatings, the thick single-layer butane-based coating and the multilayer ethane-over-butane-based coating suffered little damage from corrosion. The thick single-layer butane-based coating suffered sporadic pinpoint pitting and some small craters during the testing, and lost approximately 6 percent of its transmittance within that testing period. The multilayer ethane-over-butane-based coating offered better protection to germanium but exhibited greater loss (ie, 9 percent) in transmittance after seawater exposure.

## CONCLUSIONS

1. Massive Chalcogenide AMTIR-1 glass possesses excellent resistance to seawater corrosion, and thus does not require any protective coating on the wetted face. The projected service life of chalcogenide AMTIR-1 glass windows in the marine environment appears to be significantly longer than that of any other materials or AR coating tested.

2. Germanium coated with a thick layer of chalcogenide glass shows excellent resistance to corrosion, and has a projected service life of at least 1 year in a seawater environment. The chalcogenide glass layer, although not a true AR coating, increases the transmission of the coated window over that of bare germanium.

3. Multilayer AR Exotic Materials 40100 coating on germanium windows adequately protects the surfaces from significant corrosive action of seawater for a period of 4 months, and also maximizes the transmittance of the windows over that of bare germanium. The projected life of this coating is 6 to 12 months in a seawater environment.

4. Hard carbon coatings applied by Honeywell Inc to germanium exhibited good corrosion resistance, but suffered from an abundance of pinholes which made the otherwise extremely hard coatings permeable to seawater. They lost approximately 10 percent of their transmittance during the 4-month seawater exposure. The best corrosion resistance was achieved by a two-layer carbon coating: a soft-layer-based ethane composition superimposed on a hard-layer-based butane composition. The multilayer carbon coating on germanium acts as an antireflection coating and protects the window from significant corrosion by seawater for a period of 6 to 12 months.

5. Copper-ion leaching, forced-water circulation, and fresh-water rinsing have the definite positive effect of decreasing biofouling on submerged windows.

## RECOMMENDATIONS

Applied research on the prevention of corrosion to wetted surfaces of thermal imaging system windows in the marine environment should focus on the development of one or all of the four prime window materials and coating candidates mentioned above. More extensive testing is necessary to weigh the advantages and disadvantages of each material that is a candidate for Fleet use.

Antifouling apparatus, such as a copper-ion source or a water jetting mechanism, should be incorporated in the design of the window housings to discourage biofouling on the window.

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## 1. INTRODUCTION

Electro-optical systems operating in the 0.3-to-0.8- $\mu\text{m}$ -wavelength range have augmented man's sense of vision by allowing the viewing of objects at illumination levels which are below the threshold of unaided vision. These systems also extend man's presence to locations which are inaccessible or hazardous. Unfortunately, systems operating in the visual spectrum of light often are limited by the same environmental parameters that limit unaided human vision, such as total darkness, haze, or fog. Furthermore, unless objects are well illuminated and their surface reflectivity differs sufficiently from the background, the objects will probably escape detection.

There are, however, approaches for the detection and classification of distant objects which do not rely on reflection and reflectivity differences on surfaces in the visual spectrum. One of these approaches does not require any illumination for detection and classification of objects. This approach relies on thermal self-emission and emissivity differences of objects which produce thermal images in the viewing system.

The thermal imaging system relies for its operation on thermal energy patterns generated by all objects whose temperature is above absolute zero. The differences in effective temperatures of a thermal scene correspond in a large degree to the reflectivity differences in a visual scene and thus allow transfer of visual concepts to thermally imaged scenes.

Mechanical scanning devices which convert thermal radiation to visible radiation in real time as presented on a television screen are defined as FLIRs (forward-looking infrared). This report focuses on materials used for windows for FLIRs operating in a marine environment.

## 2. BACKGROUND

To date, the major applications of FLIRs have been for military uses. However, as mass production for the military causes the price of FLIRs to decrease, they will become attractive for nonmilitary uses. Some potential nonmilitary uses are thermal pollution surveys, forest fire detection and fighting, preventive maintenance, inspection of machinery, crime prevention, and air-sea rescue. The popularity of thermal imaging systems over passive electro-optic imaging devices operating in the visible light spectrum is due to the ability of thermal imagers to provide superior images over a wider range of atmospheric and illumination conditions (ref 1).

Because of processes that affect the passage of thermal radiation through the terrestrial atmosphere, there are two primary openings available in the atmosphere transmission of radiant energy. These are the 3.5-to-5 and 8-to-14- $\mu\text{m}$ -wavelength bands.

The 8-to-14- $\mu\text{m}$ -wavelength window is preferred by FLIR designers for several reasons. Haze attenuates the 3.5-to-5- $\mu\text{m}$  band more than the 8-to-12- $\mu\text{m}$  band. Furthermore, the ratio of thermal sensitivity of a system is higher in this band, and the peaks of radiant energy emitted by objects at ambient terrestrial temperatures are centered in this band.

There are many feasible approaches to the design of thermal (IR) imagers; however, experience has shown that only two of them provide cost-effective solutions to the thermal

imaging requirements. These are the inexpensive, low-performance, pyroelectric Vidicon thermal imagers; and, for applications requiring maximum performance, the serially scanned, cryogenically cooled array of photon detectors that have been found to provide the best visual analog of the thermal image on the television tube.

There are many potential applications of IR imagers in the marine environment. These include the military applications of detection and classification of surface and airborne targets; fire control of conventional weapons and guidance of rockets; as well as the civilian applications of sea search and rescue, firefighting on ships and off-shore platforms, detection of thermal or chemical pollution, and many industrial applications. In general, the utilization of thermal imagers in the marine environment is expected to have the same impact on operations at sea as radar and sonar had several decades ago.

### 3. MATERIALS CONSIDERATIONS FOR IR WINDOWS

Of primary concern to the designer of an IR imaging system for the marine environment is selection of window material. This selection must be based on an evaluation of both optical and mechanical characteristics (ref 1). Because the imaging system is primarily an optical system, the window must satisfy optical lens criteria, such as transmissivity to the proper wavelengths of IR emission, a suitable index of refraction, and stability of optical properties with variations in temperature. In addition, the window must protect the fragile and sensitive imager components from a hostile external environment. Thus it must possess acceptable mechanical strength, hardness, and scratch and fracture resistance, as well as be insoluble in seawater and be resistant to corrosion.

The principal selection criterion must be the ability to transmit IR radiation with a minimum of absorption. As mentioned above, transmission in the 8-to-14- $\mu$ m-wavelength range is the most desirable for marine applications because the peaks of ambient energy emitted by objects at ambient terrestrial temperatures are centered in this band. Another desirable optical characteristic is a high refractive index that does not change with temperature nor with wavelength (zero dispersion). The high refractive index is necessary to minimize lens curvature and thickness. The low thermal coefficient for refractive index prevents aberration, unbalancing, and changes in focal length as the temperature changes. Low dispersion will minimize chromatic aberration.

There are several mechanical properties that directly affect the optical performance of an IR window. There should be a low coefficient of thermal expansion so that the window shape and dimensions do not change with changes in temperature. This will prevent aberration unbalancing and changes in focal length. In addition, it will minimize the magnitude of stresses generated in the window by differences in thermal expansion between the window and the metallic mounting. The material surface must be compatible with antireflective coatings (ie, good adherence) so that the surface reflection losses can be minimized. The window material should also have high surface hardness and scratch resistance to prevent degradation of the lens surface. Insolubility in seawater and corrosion resistance are also important for preventing degradation in marine environments.

<sup>1</sup>Stachiw, J.D., and D.L. Endicott Jr., Material and Design Considerations for Thermal Imager Windows in Marine Service, proceedings of Oceans '79, San Diego, CA, September 1979.

The structural integrity of the housing that contains the thermal imaging system depends on the structural integrity of the window. It must have high mechanical strength, especially for those windows exposed to hydrostatic pressure. High mechanical strength also allows the window to be relatively thin and therefore more transmissive to infrared radiation. Corrosion resistance, in addition to preventing optical degradation of the external surface, is of importance in maintaining the sealing of the internal components from seawater. Scratch resistance is of importance because most IR materials are quite brittle and notch-sensitive. Tensile strength can be reduced as much as 75% by a surface scratch. Finally, the window must be capable of withstanding thermal shocks, such as submersion in cold seawater after exposure to elevated air temperatures, without fracturing or initiation of cracks.

With all of these criteria considered, it must now be said that no ideal material has yet been found which satisfies all of the parameters mentioned. The intent of the five stages of testing spanning three years (1977-1980), which are described in this paper, was to define the most suitable materials and coatings within the given parameters for a submarine-mounted thermal imager.

#### 4. TESTING BASED ON DESIGN CRITERIA

There were five phases of testing. Each phase was conducted by utilizing the findings of the previous test phases and seeking to improve on the performance of previous specimens. The testing consisted, in its most essential form, of the immersion of test specimens in ocean water. This was conducted at two separate NOSC testing locations. The individual locations and test procedures will be described below.

The first phase of testing (ref 2) took place at the NOSC Oceanographic Tower, which is located in the Pacific Ocean 1 mile west of the Pacific Beach community of San Diego. The types of specimens tested were germanium, zinc selenide, quartz, and Teflon, some coated and some bare. These specimens are listed among the comprehensive tables 1 through 5.

In one part of the testing, right cylindrical disc samples (3.00-inch dia X 0.25-inch thickness) were used. These were clamped by means of flat stainless-steel ring clamps and rubber gaskets bolted into an acrylic holder. Some of the specimens had copper or brass retaining rings as part of an antifouling test, and one specimen had an acrylic cover with vent holes over a copper retaining ring (see section 5, FINDINGS, for results). The samples were then submerged in seawater for varying testing periods.

In another part of the first phase of testing, three mockups of an actual, full-sized spherical IR window design configuration were tested to see what influence, if any, the IR geometry would have on fouling. One of the models consisted of a glass dome mounted on acrylic with no protection. The other two models each had a protective envelope on the baseplate which surrounded the glass dome. One featured all-stainless-steel construction, while the other had both the protective envelope and the top plate for the base made from copper. All three models were lowered 20 feet below the surface, and their rate and degree of fouling were monitored.

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<sup>2</sup>NOSC Technical Note 121, Undersea Testing of IR AR Coating and IR Materials (Dark Eyes), by J.N. Ferrer, 23 March 1977.

Sample Designation	Test Phase	Substrate Material	Manufacturer	Primary Fouling Protection
46	II	Germanium	Exotic Materials	Electric current
47	II	Germanium	Exotic Materials	None
48	II	Germanium	Exotic Materials	None
49	II	Germanium	Exotic Materials	Forced circulation of seawater
50	II	Germanium	Exotic Materials	Forced circulation of seawater
54	II	AMTIR-I chalcogenide glass	AMTIR	None
55	II	AMTIR-I chalcogenide glass	AMTIR	None
56	II	AMTIR-I chalcogenide glass	AMTIR	Forced circulation of seawater
57	II	AMTIR-I chalcogenide glass	AMTIR	Forced circulation of seawater
58	III	AMTIR-I chalcogenide glass	AMTIR	Fresh water rinsing
59	IV	AMTIR-I chalcogenide glass	AMTIR	Forced circulation of seawater
60	IV	AMTIR-I chalcogenide glass	AMTIR	Forced circulation of seawater
--	I	Teflon disc	Fluorocarbon (machine finish)	Brass ring container around front surface, open to sea
GA	I	Germanium	NELC	None
QA	I	Quartz	Optical Industries Inc	Copper 1/4-in.-thick ring retainer below plexiglass with four 3/4-in.-diameter holes
QB	I	Quartz	Optical Industries Inc	Cu ring retainer around front surface, open to sea
QC	I	Quartz	Optical Industries Inc	Brass ring retainer around front surface, open to sea
QD	I	Quartz	Optical Industries Inc	None
ZA	I	Zinc selenide	Raytheon: ZnSe; PTR	None
ZG	I	Zinc selenide 'improved'	Optics: optical finish Raytheon	None

Table 1. Competitive materials, uncoated.

Sample Designation	Test Phase	Substrate Material	Coating		Manufacturer	Primary Fouling Protection
			Sea Face	Dry Face		
11	II	Germanium	AR-XF 27	AR-XF 27	Optic Electronic	AR coating
12	II	Germanium	AR-XF 27	AR-XF 27	Optic Electronic	AR coating
13	II	Germanium	AR-XF 27	AR-XF 27	Optic Electronic	Forced circulation of seawater
14	II	Germanium	AR-XF 27	AR-XF 27	Optic Electronic	Forced circulation of seawater
15	III	Germanium	AR-XF 27	AR-XF 27	Optic Electronic	Fresh water rinsing
20	III	Germanium	AR-XF 27	AR-XF 27	Optic Electronic	Electrical current
32	II	Germanium	AR-40105*	None	Exotic Materials	Electrical current
34	II	Germanium	AR-40105*	None	Exotic Materials	AR coating
35	II	Germanium	AR-40105*	None	Exotic Materials	AR coating
36	II	Germanium	AR-40105*	None	Exotic Materials	Forced circulation of seawater
37	II	Germanium	AR-40105*	None	Exotic Materials	Forced circulation of seawater
39	III	Germanium	AR-40105*	None	Exotic Materials	Fresh water rinsing
71	III	Germanium	SLAR	None	Optical Coating Laboratory Inc	Fresh water rinsing
72	III	Germanium	SLAR	None	Optical Coating Laboratory Inc	Fresh water rinsing
73	III	Germanium	SLAR	None	Optical Coating Laboratory Inc	Fresh water rinsing
ZH	I	Zinc selenide	Dielectric hard AR (I <sub>1</sub> )	None	Raytheon	Inert, hard AR coating
ZI	I	Zinc selenide	Dielectric hard AR (I <sub>2</sub> )	None	Raytheon	Inert, hard AR coating

\*Exotic Materials AR coating 40105 was mislabeled as 40104 in previous test reports (ref 3, 4 and 5).

Table 2. Single-layer AR coatings for germanium and zinc selenide.

Sample Designation	Test Phase	Substrate Material	Coating		Manufacturer	Primary Fouling Protection
			Sea Face	Dry Face		
63	III	Germanium	AR-40100	None	Exotic Materials	Fresh water rinsing
64	III	Germanium	AR-40100	None	Exotic Materials	Fresh water rinsing
65	IV	Germanium	AR-40100	None	Exotic Materials	Forced circulation of seawater
66	IV	Germanium	AR-40100	None	Exotic Materials	Forced circulation of seawater
74	III	Germanium	AR-XF 127	None	Optic Electronic	Forced circulation of seawater
75	III	Germanium	AR-XF 127	None	Optic Electronic	Fresh water rinsing
76	IV	Germanium	AR-XF 127	None	Optic Electronic	Forced circulation of seawater
77	III	Germanium	AR-XF 129	None	Optic Electronic	Fresh water rinsing
78	III	Germanium	AR-XF 129	None	Optic Electronic	Fresh water rinsing
80	IV	Germanium	AR-XF 204	None	Optic Electronic	Forced circulation of seawater
81	IV	Germanium	AR-XF 205	None	Optic Electronic	Forced circulation of seawater
82	IV	Germanium	AR-XF 202	None	Optic Electronic	Forced circulation of seawater
83	IV	Germanium	AR-XF 203	None	Optic Electronic	Forced circulation of seawater
84	IV	Germanium	AR-XF 203	None	Optic Electronic	Forced circulation of seawater
85	IV	Germanium	AR-XF 205	None	Optic Electronic	Forced circulation of seawater
86	IV	Germanium	AR-XF 206 chalcogenide	None	Optic Electronic	Forced circulation of seawater

Table 3. Multiple-layer AR coatings for germanium.



Sample Designation	Test Phase	Substrate Material	Coating		Manufacturer	Primary Fouling Protection
			Sea Face	Dry Face		
1	II	Germanium	Polyolefin on AR	None	Lane Instrument Co	Electric current
2	II	Germanium	Polyolefin on AR	None	Lane Instrument Co	Plastic overcoat
3	II	Germanium	Polyolefin on AR	None	Lane Instrument Co	Plastic overcoat
4	II	Germanium	Polyolefin on AR	None	Lane Instrument Co	Forced circulation of seawater
5	II	Germanium	Polyolefin on AR	None	Lane Instrument Co	Forced circulation of seawater
1-2	I	Germanium	Parylene on AR	None	NELC:AR	Plastic overcoat
G2-1	I	Germanium	Organometallic on AR	None	Union Carbide: parylene NELC	Organometallic coating
G2-2	I	Germanium	Organometallic on AR	None	NELC	Organometallic coating
G2-3	I	Germanium	Organometallic on AR	None	NELC	Organometallic coating
2H	II	Germanium	3-layer AR PE/PP/PE*	3-layer AR PE/PP/PE	Honeywell	Plastic overlay
4H	II	Germanium	3-layer AR PE/PP/PE	3-layer AR PE/PP/PE	Honeywell	Forced circulation of seawater
5H	II	Germanium	3-layer AR PE/PP/PE	3-layer AR PE/PP/PE	Honeywell	Electric current
8H	II	Germanium	1-layer AR PE/PP/PE	1-layer AR PE/PP/PE	Honeywell	Plastic overlay
9H	II	Germanium	1-layer AR PE/PP/PE	1-layer AR PE/PP/PE	Honeywell	Forced circulation of seawater
12H	II	Germanium	1-layer AR PE/PP/PE	1-layer AR PE/PP/PE	Honeywell	Electric current
13H	II	Germanium	AR, Tenite	AR	Honeywell	Electric current
14H	II	Germanium	AR, Tenite	AR	Honeywell	Electric current

\*PE: Polyethylene PP: Polypropylene

Table 4. Overcoatings on AR coatings.

Sample Designation	Test Phase	Substrate Material	Coating		Manufacturer	Primary Fouling Protection
			Sea Face	Dry Face		
23	II	Germanium	Polyethylene	None	Honeywell	Electric current
27	II	Germanium	Polyethylene	None	Honeywell	Electric current
91	V	Germanium	Carbon, V003132	None	Honeywell	Forced circulation of seawater
92	V	Germanium	Carbon, L00506	None	Honeywell	Forced circulation of seawater
93	V	Germanium	Carbon, L005022	Carbon, L005022	Honeywell	Forced circulation of seawater
94	V	Germanium	Carbon, L005094	Carbon, L005094	Honeywell	Forced circulation of seawater
95	V	Germanium	Carbon, D004232	None	Honeywell	Forced circulation of seawater
96	V	Germanium	Carbon, D004231	None	Honeywell	Forced circulation of seawater
GC	I	Germanium	Thorium fluoride (ThF <sub>4</sub> )	None	NELC: Ge, SPAWR Optical Coating Lab Inc: ThF <sub>4</sub>	Inert, hard coating

Table 5. Coatings (not AR) on bare germanium.



LRO 3006-8-78B

Figure 1. The hydraulic hoist off building 160B, pier 160, NOSC Bayside, San Diego. A test fixture is attached to the platform, with pump and manifold apparatus is visible.

The remaining phases of testing took place in San Diego Bay off Berthing Pier 160, NOSC, Bayside (ref 3, 4, and 5, and appendix A). This test site had a hydraulic hoist that could be lowered to a 35-foot depth into the bay and serve as a platform to which the test fixtures could be attached (fig 1).

The test fixtures consisted of one single and three multiple specimen holders (fig 2, 3, 4, and 5) made of polyvinylchloride (PVC). Each specimen holder had recesses into which the specimens were sealed by titanium ring clamps and rubber O-rings affixed by nylon bolts. The assembled multiple specimen fixtures also had protective acrylic plates which were held above the PVC baseplate by PVC studs and spacers.

The specimens were of the same dimensions as the cylindrical section specimens mentioned in the phase I testing. Phase II examined two substrate materials (germanium and chalcogenide glass), and antifouling methods such as forced seawater circulation and electric current heating were used. In subsequent test phases (phases III through V), the same testing setup and fixtures were used, with improved as well as new types of coatings. Each of these phases of testing was 4 months in duration, with transmittance testing being done both prior to submersion and after the 4-month testing period.

## 5. FINDINGS

Six substrate materials were tested (table 1). Two of these materials, quartz and Teflon, were used only as surfaces for fouling tests, and were not intended as actual materials for optical lenses. Of the four remaining materials for lenses, zinc selenide was discontinued as a substrate material after the first phase of testing because of the rapid deterioration that the material experienced in seawater.

The remaining materials, germanium and chalcogenide glass, each have shown both positive and negative characteristics. Germanium is the material of choice, since it is stronger, harder, more thermally conductive, and hence more resistant to fracture than the chalcogenide glass (ref 6 and 7). In addition, germanium has the major advantage of having been used in the manufacturing of thermal-imaging lenses for more than 20 years. Thus optical-grade germanium is available in many configurations at more competitive prices than many of the other IR materials (ref 1). Unfortunately, germanium has the shortcoming of being highly susceptible to seawater corrosion. The chalcogenide glass, on the other hand, has the advantage of a more thermally stable index of refraction, and it has been determined experimentally (ref 3) to have excellent corrosion resistance (fig 6). Specimens of chalcogenide AMTIR-1 glass showed no significant change in transmittance after 4 months' exposure to seawater in

<sup>3</sup> NOSC Technical Report 421, Resistance of Coated and Uncoated IR Windows to Seawater Corrosion, by J.D. Stachiw and S.L. Bertic, 15 August 1979.

<sup>4</sup> NOSC TR 572, Resistance of Coated and Uncoated IR Windows to Seawater Corrosion, Phase III, by J.D. Stachiw and S.L. Bertic, July 1980.

<sup>5</sup> NOSC TR 587, Resistance of Coated and Uncoated IR Windows to Seawater Corrosion, Phase IV, 1 October 1980.

<sup>6</sup> NOSC TR 191, Ice Formation on Germanium Windows in Marine Service, by J.D. Stachiw and D.L. Endicott Jr., 1 March 1978.

<sup>7</sup> NOSC TR 565, Germanium Optical Viewports for High Pressure Service, by J.D. Stachiw, June 1980.

San Diego Bay (fig 7). Furthermore, it has been determined experimentally that when germanium and chalcogenide glass specimens are identically exposed to sunlight, the germanium is heated to a higher temperature than the chalcogenide glass (ref 8). Germanium reaches approximately 150°F, while chalcogenide glass stays about 25° cooler. A comparison of the physical and optical properties of optical-grade germanium and chalcogenide glass may be seen in table 6.

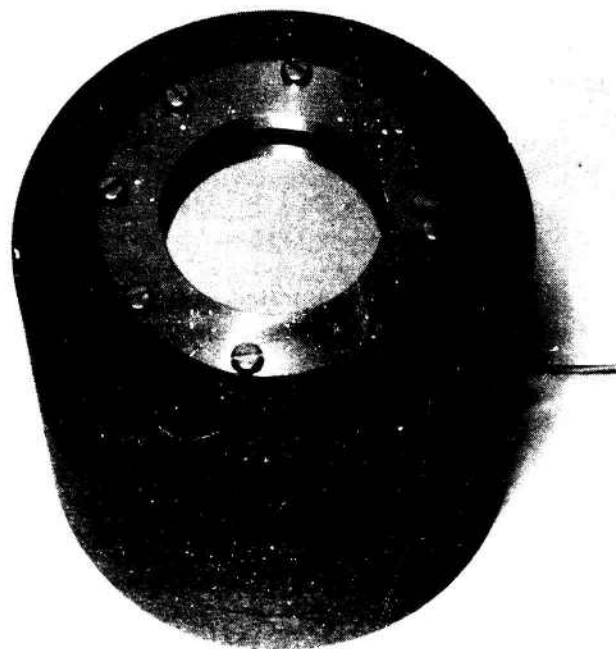
## COATINGS

Three major types of coatings were tested: antireflective (AR) coatings, protective surcoats for AR coatings, and protective coatings on bare substrate. Single- and multiple-layer AR coatings were used on germanium and zinc selenide to increase transmittance, and more importantly to protect the substrates from corrosion. Coating materials that were not

Property	AMTIR-1	Germanium
Composition	Ge <sub>33</sub> As <sub>12</sub> Se <sub>55</sub>	Ge
Transmission range	1 - 15 $\mu\text{m}$	2 - 18 $\mu\text{m}$
Refractive index (10 $\mu\text{m}$ )	2.4975	4.0025
$\Delta n/\Delta T^\circ \times 10^{-6}$	72	400
Hardness (Knoop)	170	850
Thermal expansion	$13 \times 10^{-6}/^\circ\text{C}$	$6 \times 10^{-6}/^\circ\text{C}$
Thermal conductivity (cal/s cm $^\circ\text{C}$ )	$5.5 \times 10^{-4}$	$1.4 \times 10^{-2}$
Specific heat (cal/g $^\circ\text{C}$ )	$7.2 \times 10^{-2}$	$7.4 \times 10^{-2}$
Density g/cm <sup>3</sup>	4.40	5.33
Modulus of rupture, typical annealed (psi)	2500	10 000
Glass transition temperature (T <sub>g</sub> $^\circ\text{C}$ )	405	937 $^\circ\text{C}$ (MP)
Upper use temperature ( $^\circ\text{C}$ )	310	200
Dispersion		
3.5 $\mu\text{m}$	192	102
8 - 12 $\mu\text{m}$	127	970
Reflectivity	18.3%	36%
Transmission maximum (uncoated)	69%	53%
Absorption at 10.6 $\mu\text{m}$ cm <sup>-1</sup>	0.02	0.02
Poisson's ratio	0.27	0.25
Compressive strength (psi)	30 000	60 000
Modulus of elasticity (psi)	$0.319 \times 10^7$	$1.49 \times 10^7$

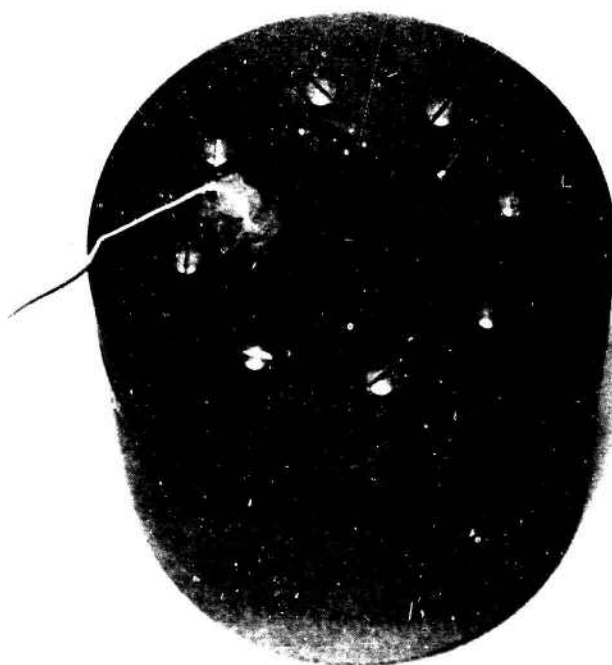
Table 6. Comparison of physical and optical properties of optical-grade germanium and chalcogenide glass.

<sup>8</sup> Private communication from T.J. Moravec, Honeywell Technology Center, Bloomington, MN, 14 May 1980.



(a)

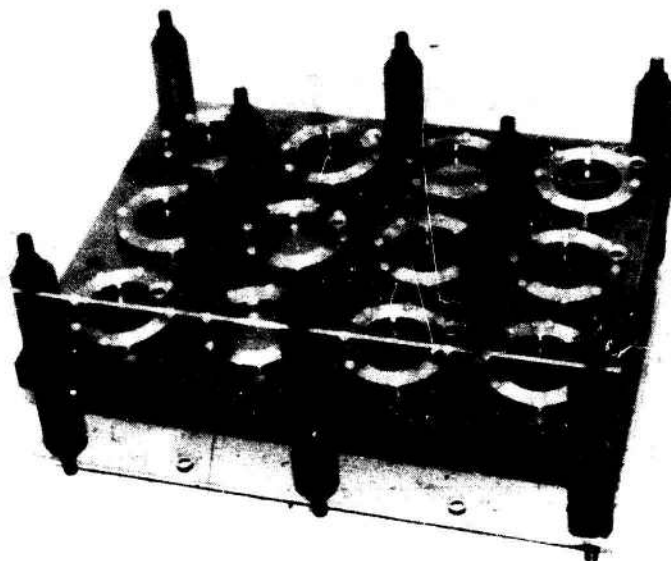
LRO 2630-7-78



(b)

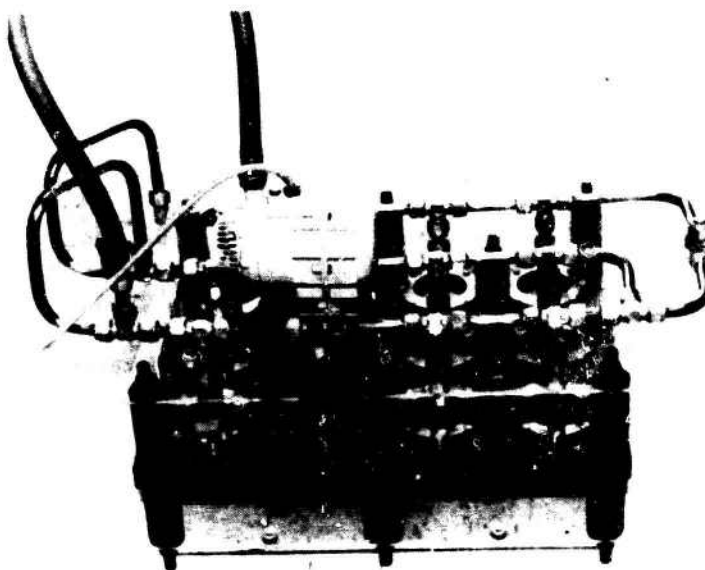
LRO 2629-7-78

Figure 2. The single-specimen test fixture, showing anterior and posterior views. The fixture was equipped with electrical contacts for applying electrical current to the body of the window that raised its temperature above the ambient temperature of seawater.



LRO 2675-7-78B

Figure 3. The multiple-specimen test fixture A with no provision for forced seawater circulation.



LRO 2676-7-78B

Figure 4. The multiple-specimen test fixture B with a pump and manifold apparatus to provide forced seawater circulation to the specimens.

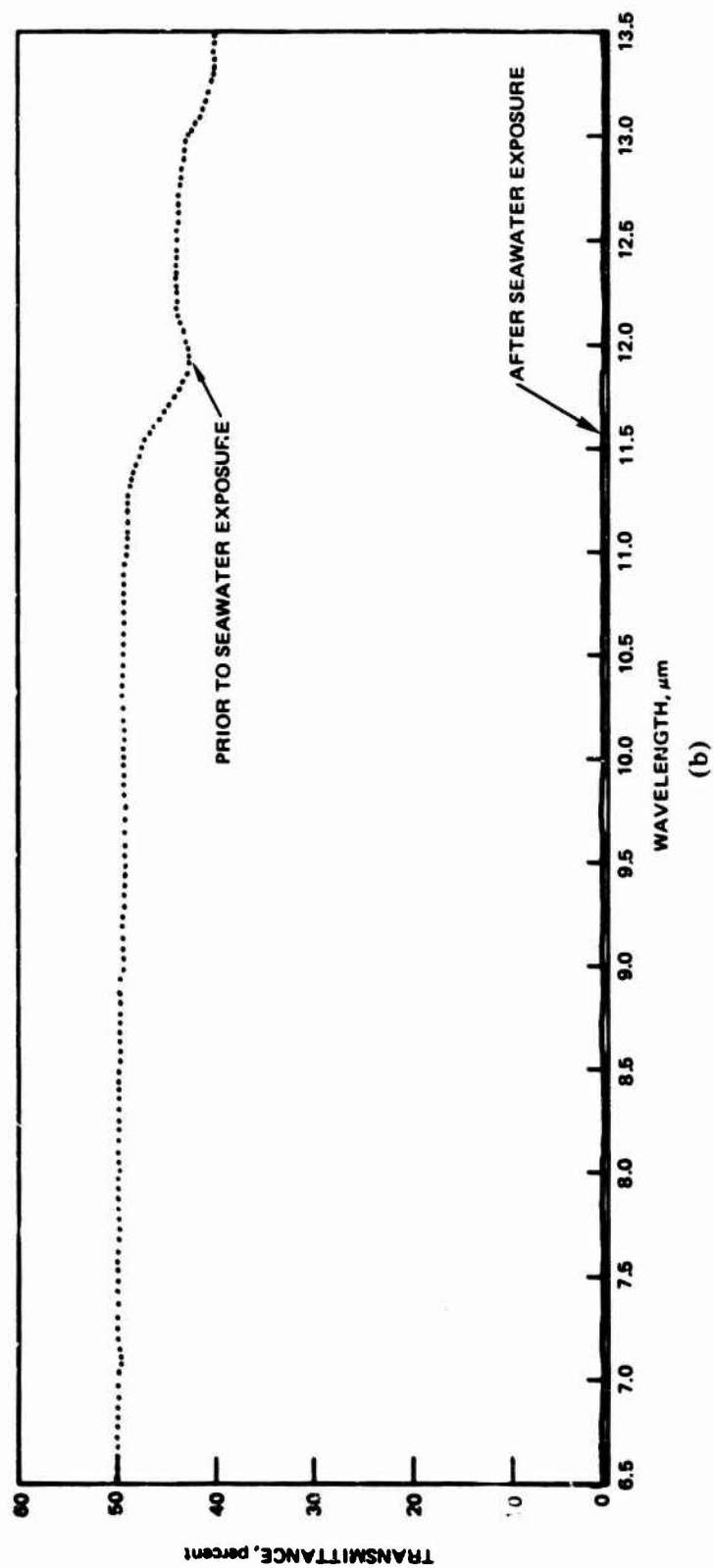


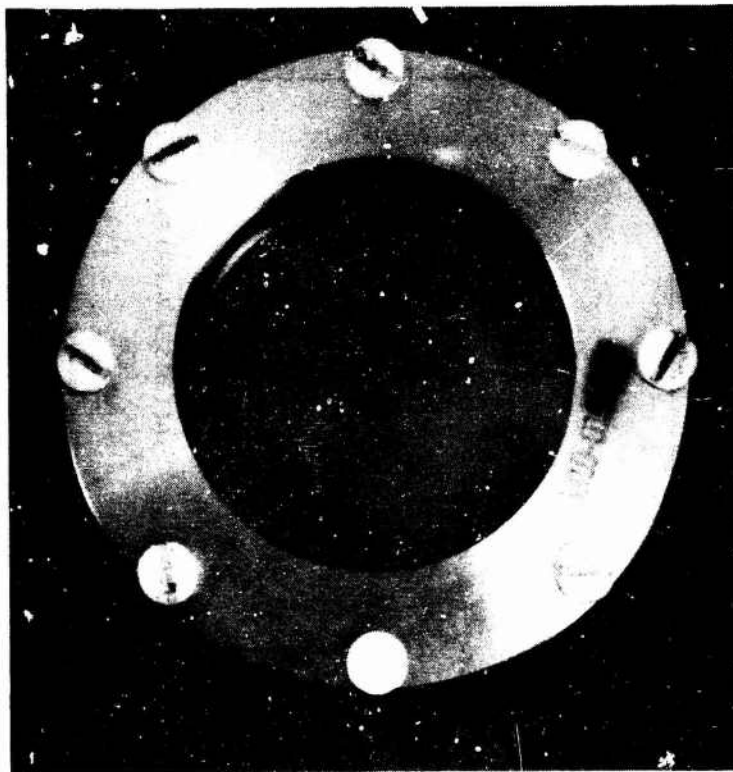
Sample #95  
(a)

Polyethylene on ethane

Figure 5a-b. (a) Polished germanium specimen after 4-month exposure to seawater in San Diego Bay; (b) the corrosion of the wetted surface on the specimen dramatically decreases the transmittance







LRO 1761-6-808

Figure 6. A specimen of chalcogenide AMTIR-1 glass after 4 months' exposure to seawater in San Diego Bay.

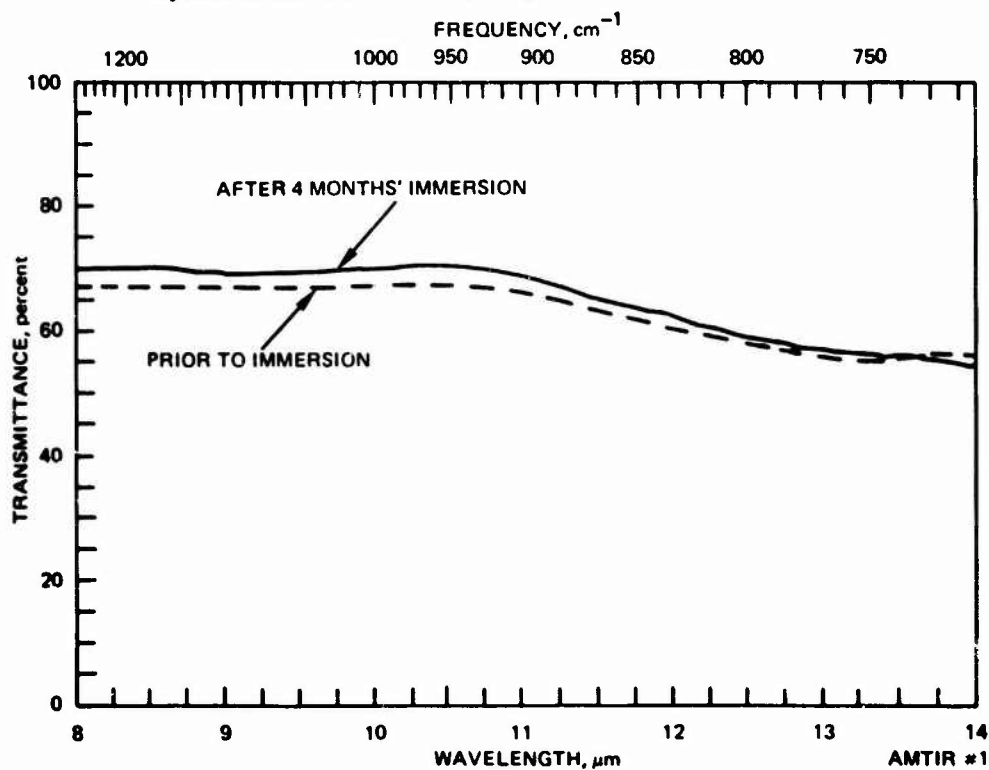


Figure 7. The transmittance of a 0.25-inch-thick specimen of chalcogenide AMTIR-1 glass both prior to and after 4 months' exposure to seawater in San Diego Bay.

AR were intended solely for corrosion protection, even though they exhibit some antireflective properties. These were tried both with and without additional AR coatings to give a greater number of options for protection. A complete listing of coatings is included in tables 1 through 5 of this report. There were four primary indications of coating failure: pitting, peeling, dissolution, and decrease in transmittance.

### **Pitting**

The result of pinholes or weak spots in the coating, which usually indicated uneven or incomplete coating application. The pitting varied in intensity from pinpoint pits (fig 8), which are small (usually <0.01-inch-dia) holes through the coating to the surface of the substrate; to small craters (fig 9), which are larger areas approximately 0.05 inch in diameter or more, where the seawater has acted through a pinhole in the coating actually to corrode a substantial amount of the substrate. Pitting was accelerated in some instances by forced circulation of seawater (fig 10).

### **Peeling**

in essence, nonadhesion of the coating to the substrate. When the coating fails to adhere properly and peels away from the substrate surface, it enables seawater to seep between the coating and the substrate and act upon the substrate (fig 11).

### **Dissolution**

Appears as the discoloration of coatings which, upon closer inspection, is revealed to be the widespread leaching away of layers composing the antireflection coatings; some layers remain intact below, and continue to seal the substrate from seawater corrosion (fig 12). This widespread leaching out of coating layers decreases the optical transmission more than does the highly localized formation of pits or craters. From a maintenance viewpoint, however, the leaching out of coating is a much-less-destructive form of corrosion. During the refinishing of such windows, less (or even no) germanium substrate need be removed prior to recoating, as is the case when the substrate has been pitted.

### **Transmittance Loss**

Since transmittance measurements were made both prior to and at the conclusion of testing, any change in transmissivity of the specimen could be noted (fig 13). Usually, coating breakdown is indicated by a drop in transmittance.

Most of the coatings tested showed one, or a combination of several, of the indications of failure specified above. However, some performed notably better than the average.

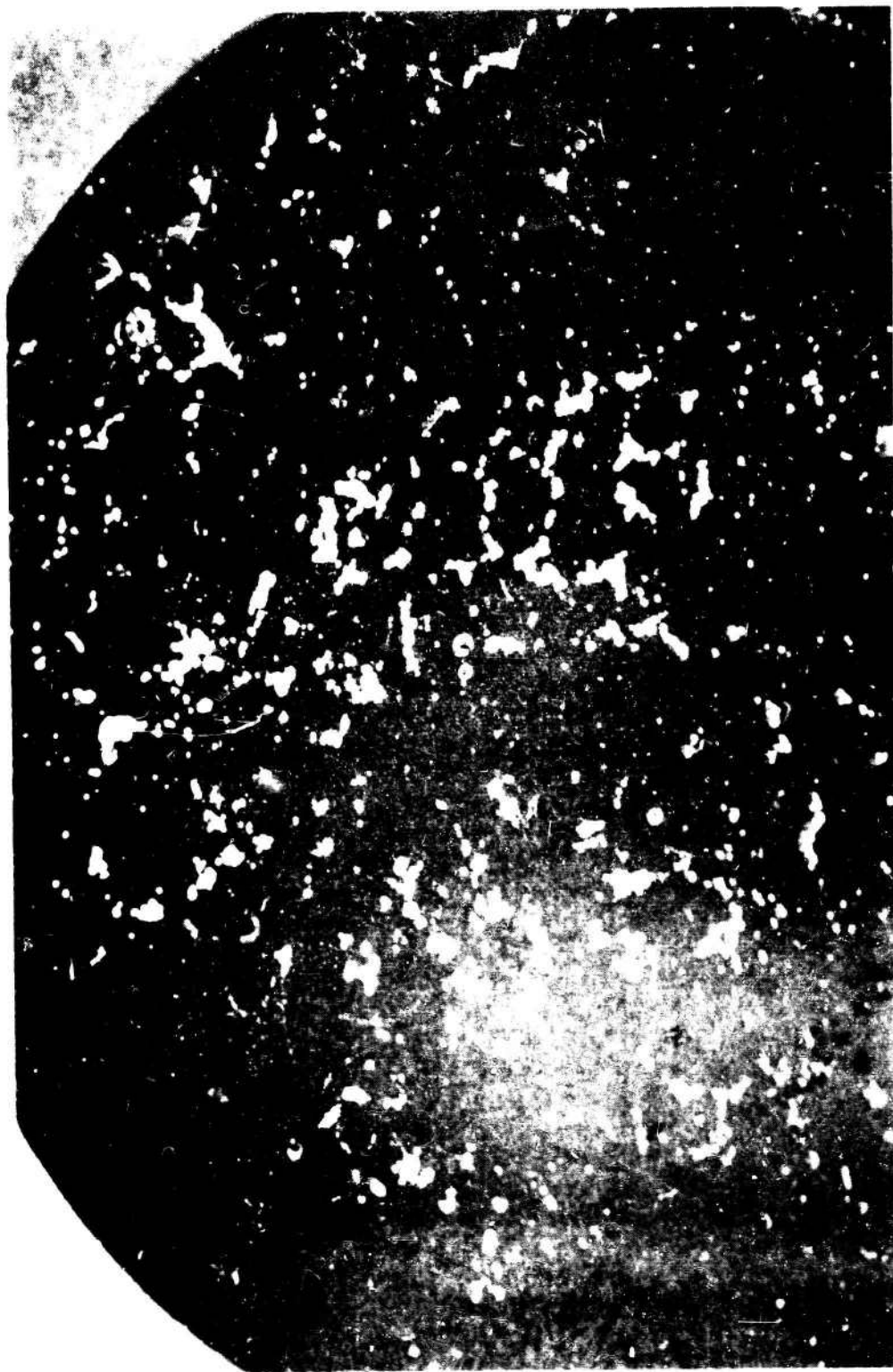
The most durable single-layer AR coating proved to be the Exotic Materials 40105 (fig 14), which was first tested in phase II. This coating had a very flat transmittance-versus-wavelength curve over the 7-to-13- $\mu$ m spectral range (fig 15). The transmittance decreased after exposure to seawater for 4 months by a maximum of 5 percent at 10- $\mu$ m wavelength.



9000A, butane, very hard.

Sample #91

Figure 8. A coated germanium specimen showing typical pinpoint pitting distributed across the specimen's surface: butane-based carbon coating (Honeywell V003132) of 0.9- $\mu$ m thickness after 4 months of seawater immersion.



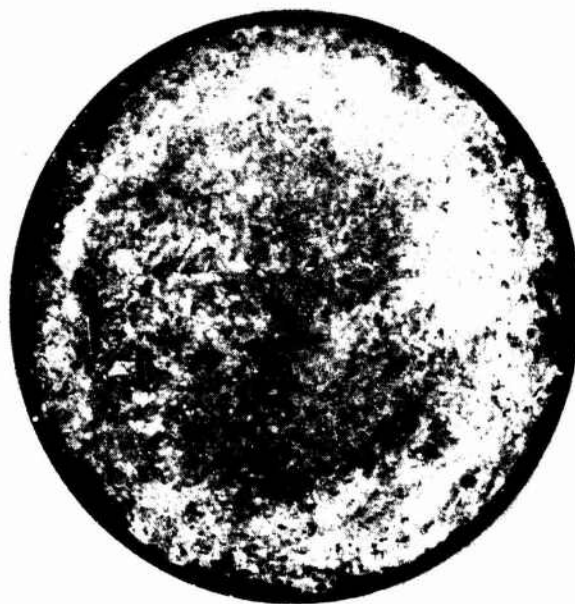
C<sub>4</sub> H<sub>10</sub> 5800A, very hard.

Sample #94

Figure 9. A coated germanium specimen showing substantial pitting which has extended into cratering; butane-based carbon coating (Honeywell L005094) of 0.5- $\mu$ m thickness after 4 months of seawater immersion.



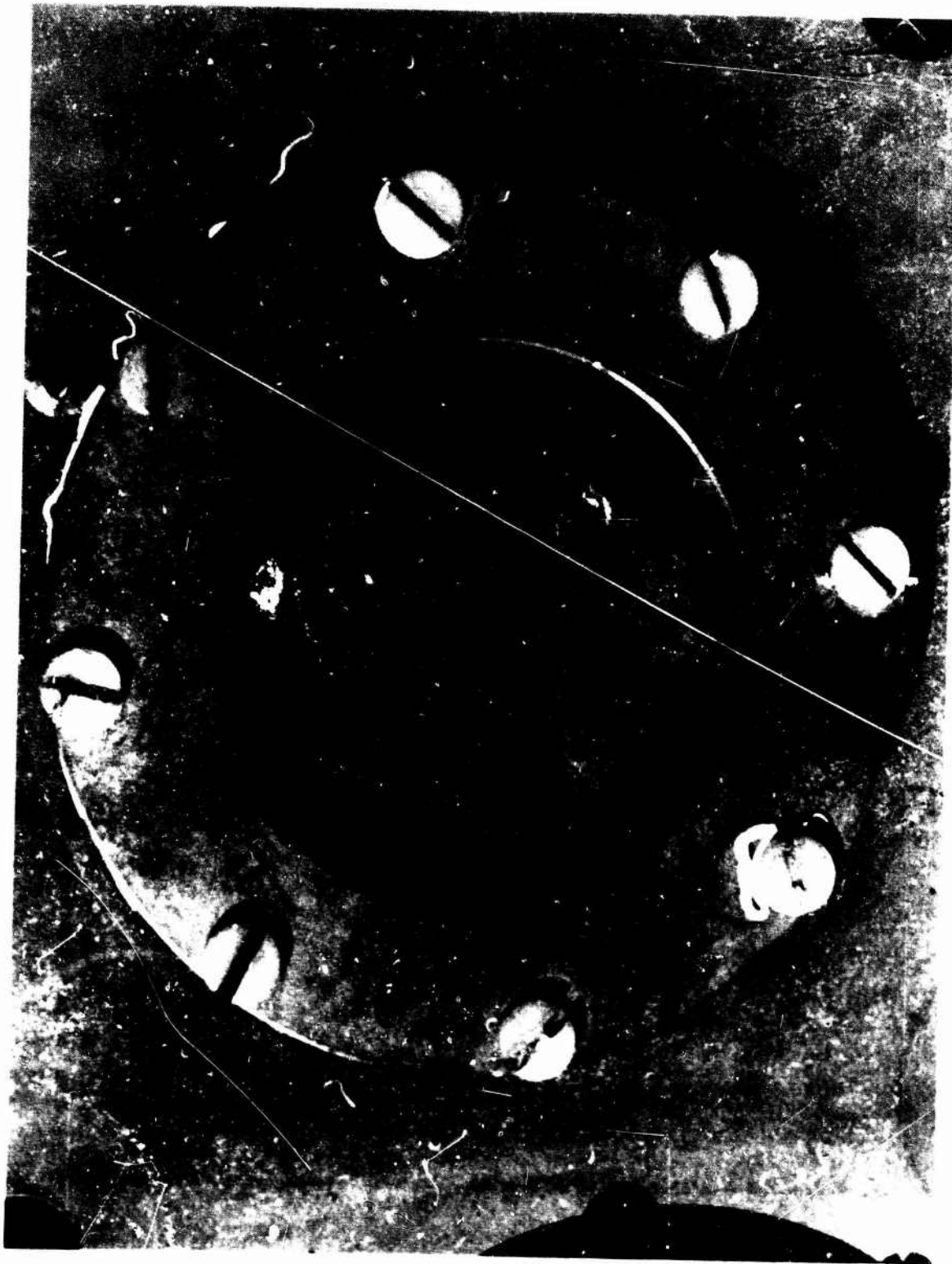
No forced circulation



Forced circulation

LRO 1791-G-80B

Figure 10. Two specimens with the same type of AR coating tested for 4 months over the same time period, showing the acceleration of coating breakdown caused by forced seawater circulation.



LRO 4707-12-78B

Figure 11. A coated specimen (after 4 months of testing) whose plastic coating has torn and peeled away from the substrate, leaving the substrate exposed to corrosion by seawater.



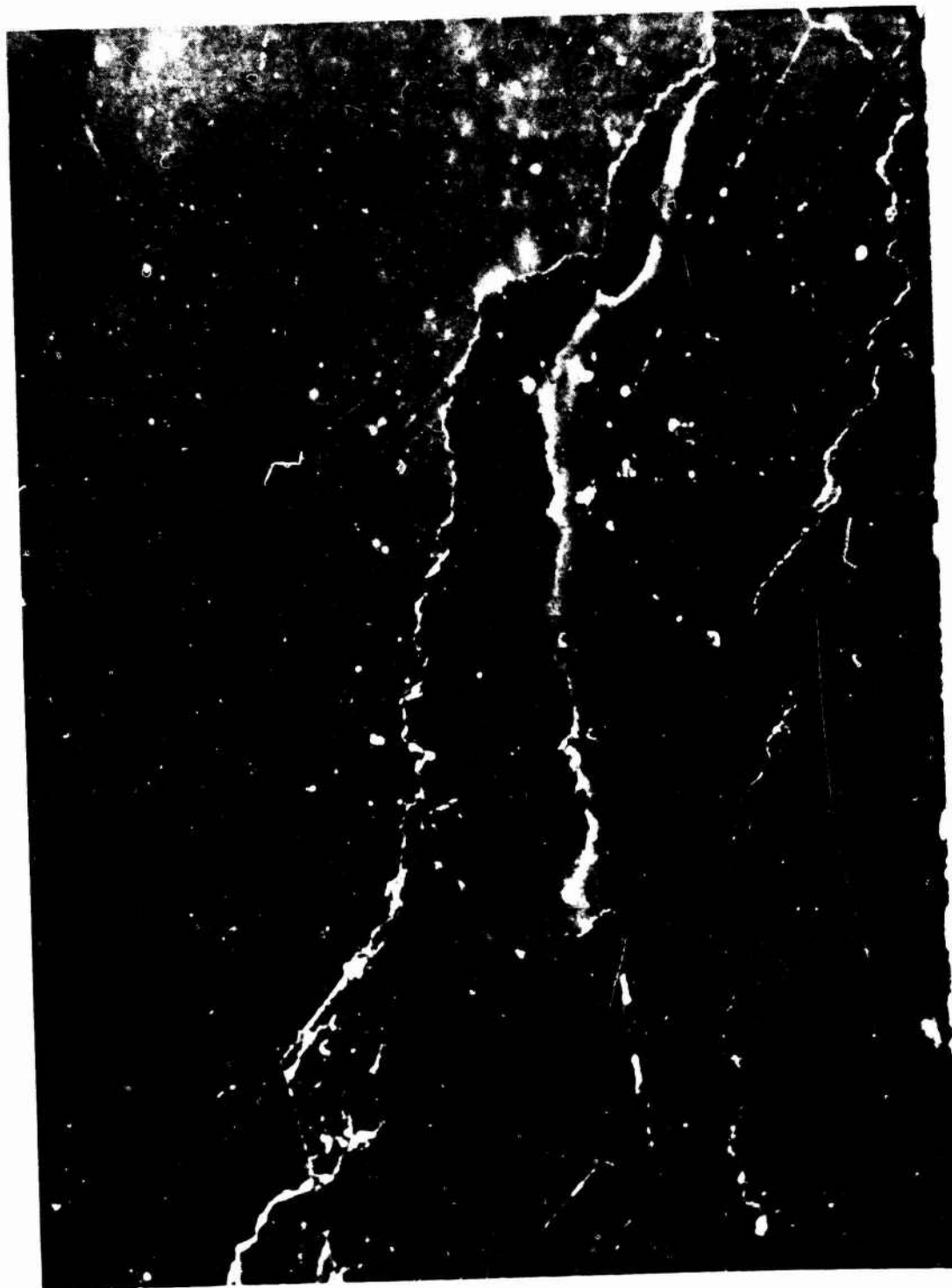


Figure 12. A coated specimen displaying characteristic edge lines of layers in a multilayer AR coating (Optic Electronic XF127) which has been partially leached away by seawater.



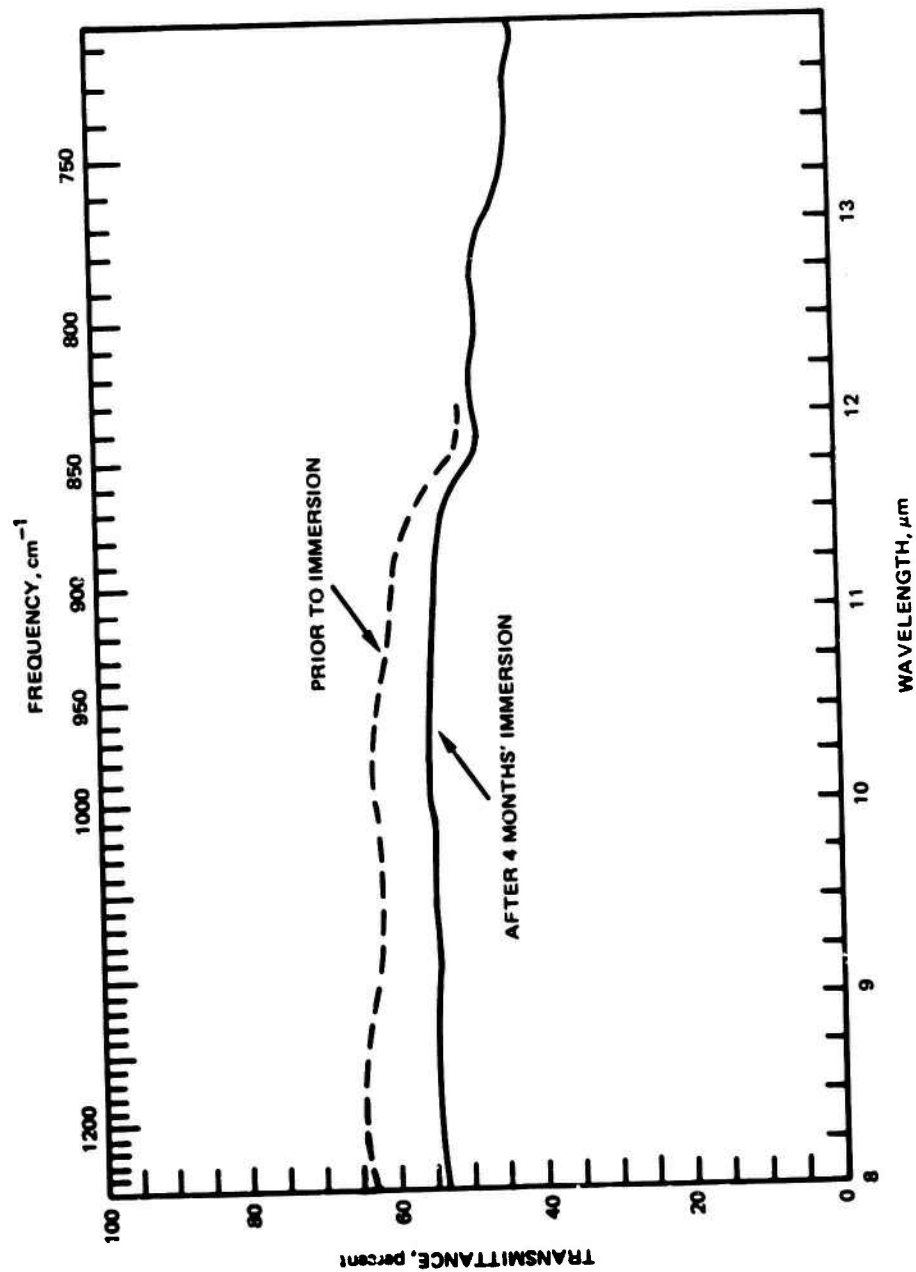
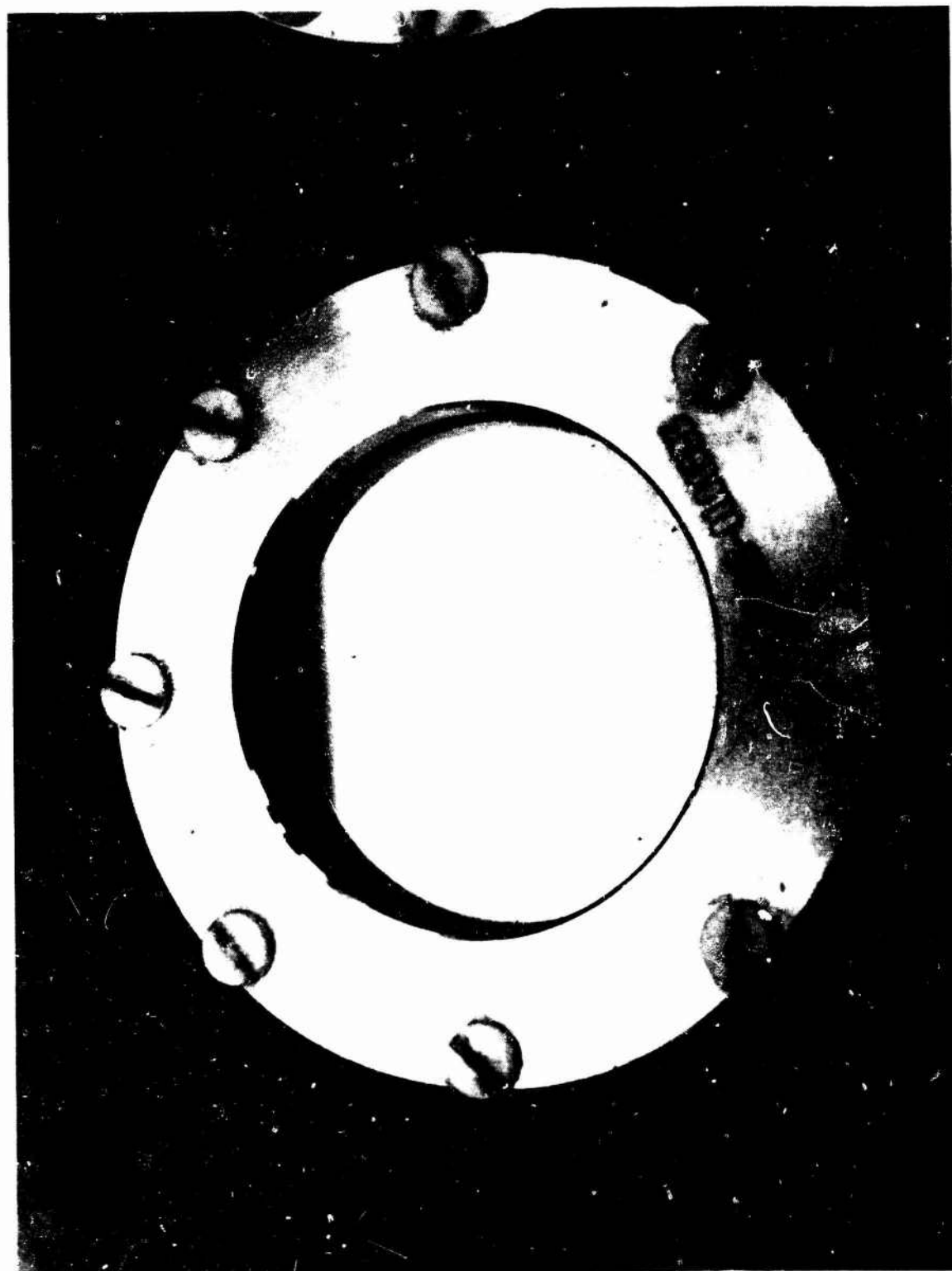


Figure 13. The transmittance of a 0.25-inch-thick germanium specimen with a nondurable multilayer AR coating (Optic Electronic XF127) on the sea face, both prior to and after 4 months' exposure to seawater in San Diego Bay. This plot illustrates the change in transmittance of a specimen which may occur during a testing period.



LRO 4098-9-79B

Figure 14. A germanium specimen with a protected monolayer AR coating (Exotic Materials 40105) after 4 months' exposure to seawater in San Diego Bay.

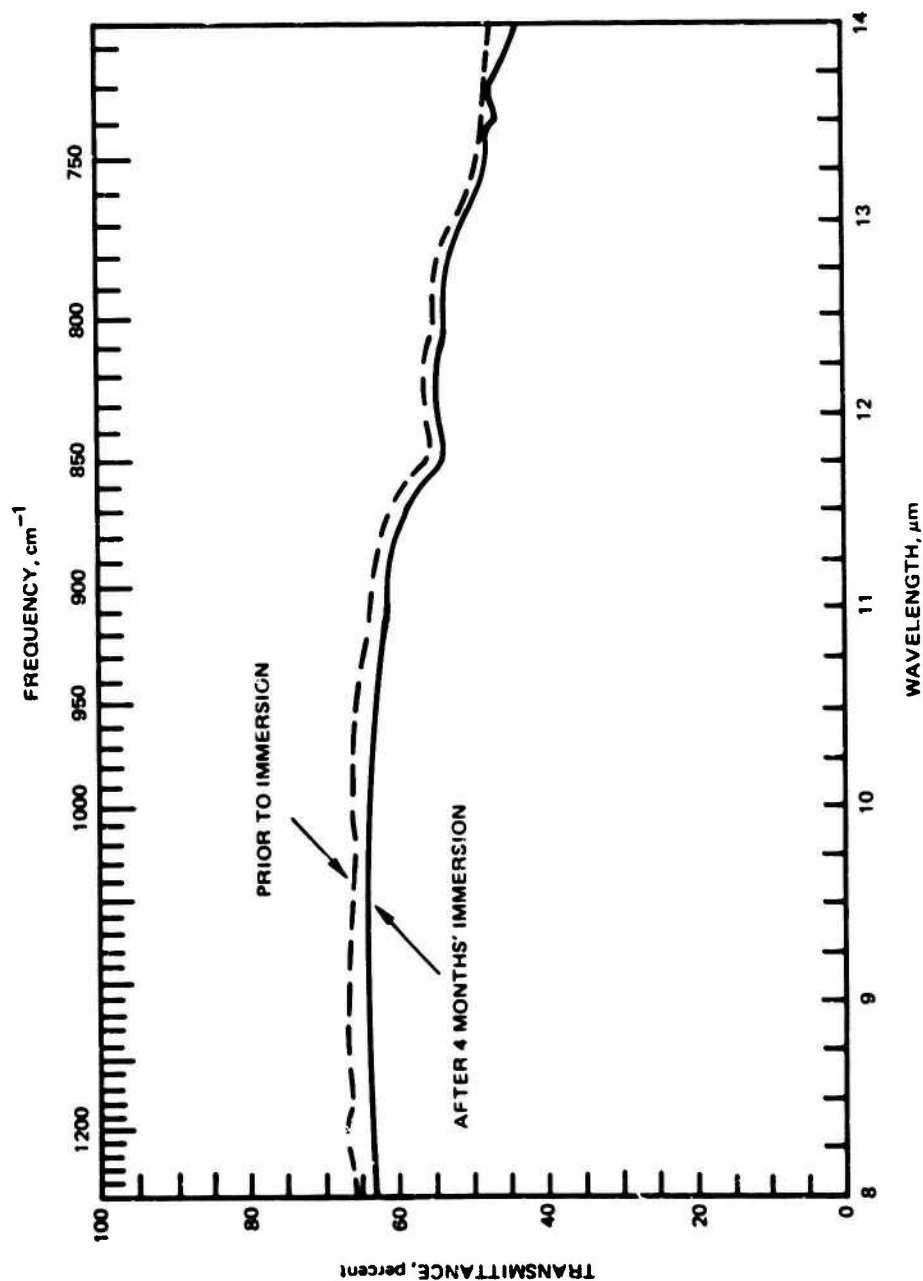


Figure 15. The transmittance of a 0.25-inch-thick germanium specimen with a protected monolayer AR coating (Exotic Materials 40105) on the sea face, after 4 months' exposure to seawater in San Diego Bay.

Generally, the multilayer AR coatings were more durable than the single-layer coatings. Of these, the Exotic Materials 40100 multilayer durable coating (fig 16) performed best. Specimens with this coating were tested in phase III and phase IV of the series, and in both cases the coating held up better than its competitors. The transmittance of a specimen coated on one side with EM 40100 was 60 to 65 percent in the 8-to-11.5- $\mu\text{m}$  range, sloping off to 50 percent at 14  $\mu\text{m}$  (fig 17). From the testing, it is apparent that this coating will protect germanium at least 6 months, and maybe even 12 months, without any significant decrease in its antireflective properties.

Of the coatings which are primarily protective in nature, there are two types that are very promising. One is the Optic Electronic XF206 (fig 18), which is a thick coating of AMTIR-1 chalcogenide glass ( $\text{Ge}_{13}\text{As}_{12}\text{Se}_{55}$ ). The XF206 coating is approximately 35  $\mu\text{m}$  thick, which is much thicker than the average antireflection coating, whose thickness is only on the order of several wavelengths. This coating combines the excellent corrosion resistance of the chalcogenide glass, with the strength and higher resistance to fracture of the germanium substrate. The specimen with this coating suffered no loss in transmittance during 130 days of exposure to seawater. The transmittance curves oscillated sinusoidally with wavelength, but the average transmittance for the germanium specimen coated on a single surface varied in a smooth curve from a high of 55 percent at the low end of the spectrum, to approximately 50 percent at 12  $\mu\text{m}$  (fig 19).

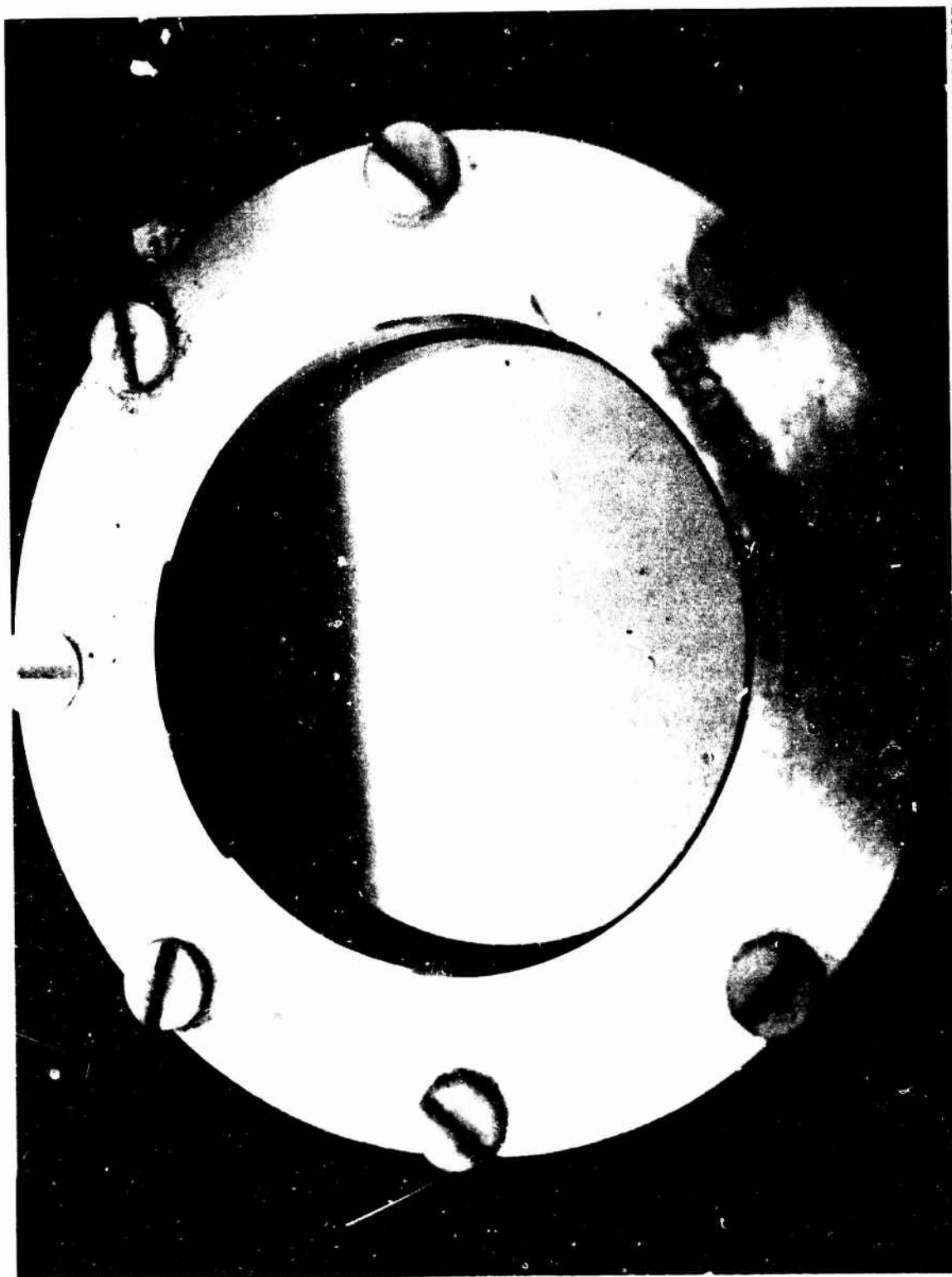
Another class of protective coatings which have potential for the seawater environment are thick (0.5-to-1.0- $\mu\text{m}$ ) carbon coatings with a diamondlike molecular structure. The superior coating among these is the Honeywell L00506 of the phase V testing (fig 20). The coating consisted of a butane-based bottom layer 0.5  $\mu\text{m}$  in thickness, covered by a 2- $\mu\text{m}$ -thick layer of soft ethane-based coating. The butane-based coating is extremely hard and scratch-resistant, but it is subject to a large number of pinholes when applied less than 1  $\mu\text{m}$  thick. Adding a top layer of ethane-based coating eliminates the pinholes without decreasing significantly the transmittance of the coated germanium specimen. The transmittance of the germanium specimen coated on a single surface decreased from 4 to 10 percent after 4 months of exposure to seawater, from a presubmersion average of approximately 54 percent (fig 21).

The Honeywell V003132 coating, which represents a 0.9- $\mu\text{m}$ -thick butane-based layer, also performed well in the testing. The specimen suffered localized pinpoint pitting and had approximately a dozen small craters after the test period of 4 months' exposure to seawater (fig 22). The germanium specimen coated on a single face suffered a transmittance loss of only 6 percent or less over the 8-to-14- $\mu\text{m}$  wavelength range after exposure to seawater (fig 23), sloping from 55 percent transmittance at 8  $\mu\text{m}$  to 44 percent at 12  $\mu\text{m}$ .

## FOULING

Fouling is the process of animal growth and/or debris from the environment adhering to the windows and degrading or completely impeding the optical performance of an enclosed imaging system. It was found experimentally that a vast number of organisms, including algae, barnacles, minute squid, coral, various worms, and the roe and larval stages of larger organisms may be deposited on the windows (fig 24). Because of this, methods to prevent biofouling from becoming established were tested on the variously coated test specimens.

Several methods of discouraging biofouling were tried during the five phases of testing, none of which provided the complete answer for the prevention of fouling. The merits and failures of each method must be weighed to determine an antifouling method that is optimal and at the same time operationally practical.



LRO 4094-9-79B

Figure 16. A germanium specimen with a durable multilayer AR coating (Exotic Materials 40100) after 4 months' exposure to seawater in San Diego Bay.

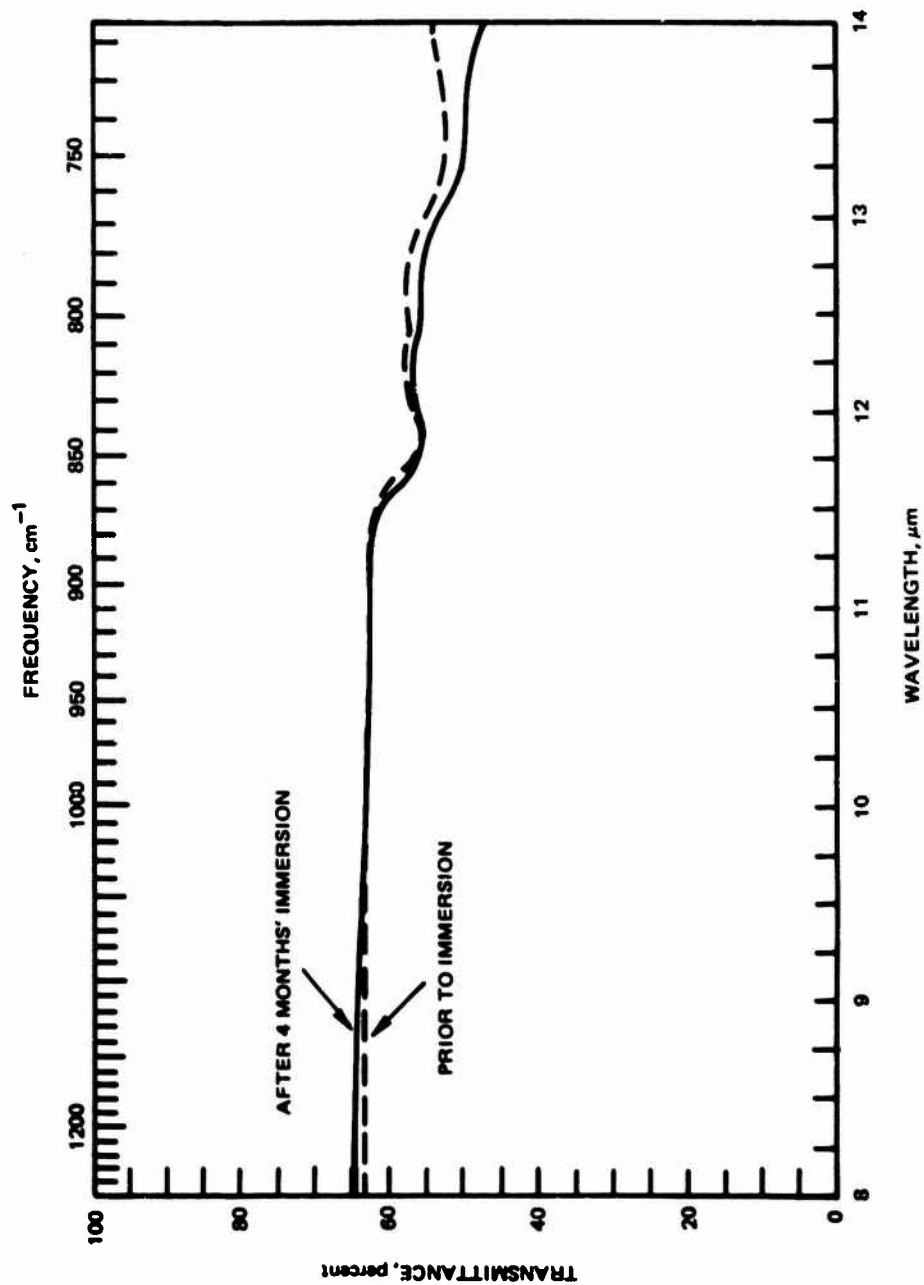
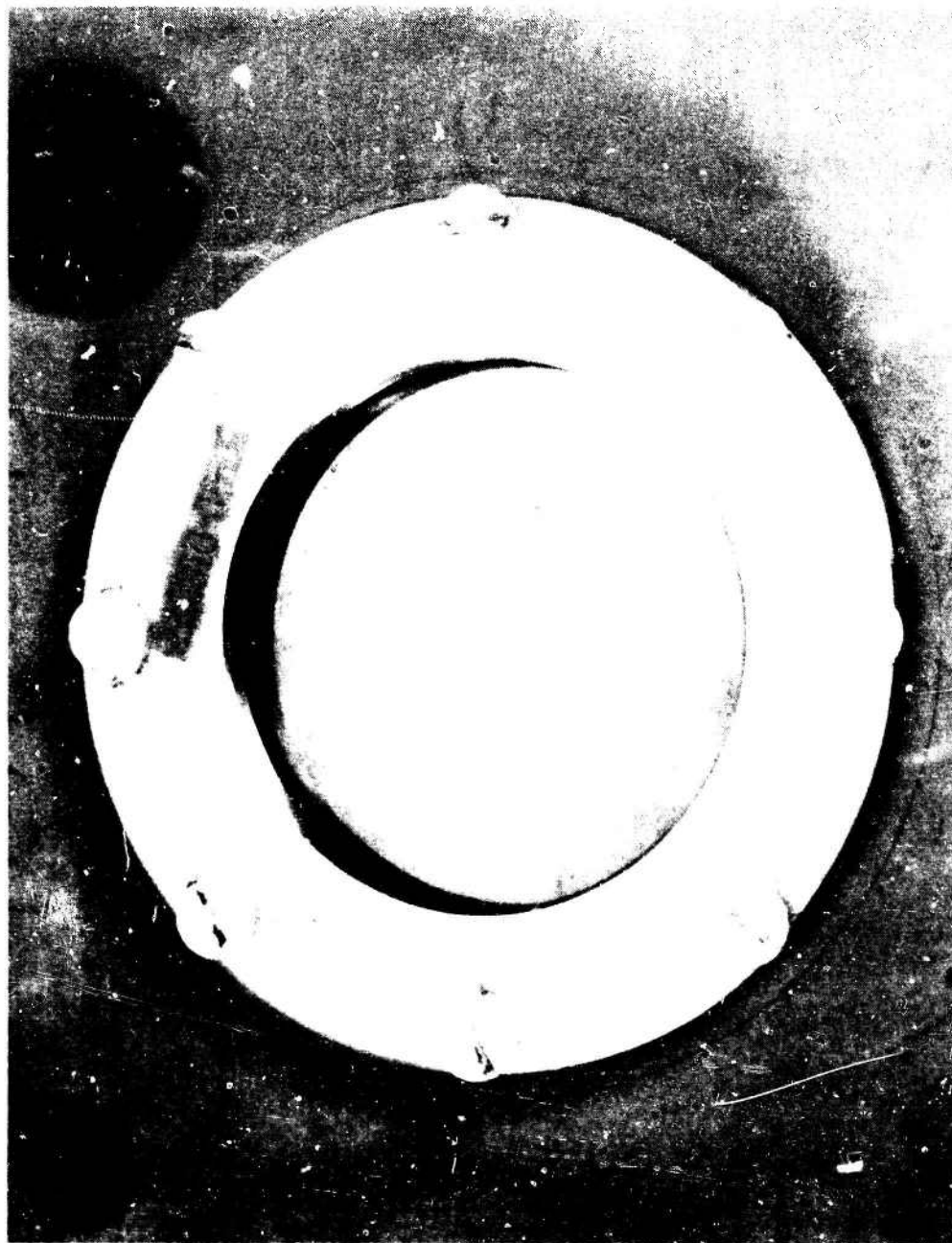


Figure 17. The transmittance of a 0.25-inch-thick germanium specimen with a multilayer durable AR coating (Exotic Materials 40100) on the sea face, both prior to and after 4 months' exposure to seawater in San Diego Bay.



LRO 1754-6-80B

Figure 18. A germanium specimen with a thick chalcogenide glass coating (Optic Electronic XF206) after 4 months' exposure to seawater in San Diego Bay; the single missing patch of coating in the center of the specimen was caused by rough handling during cleaning of the test rack.

XF206

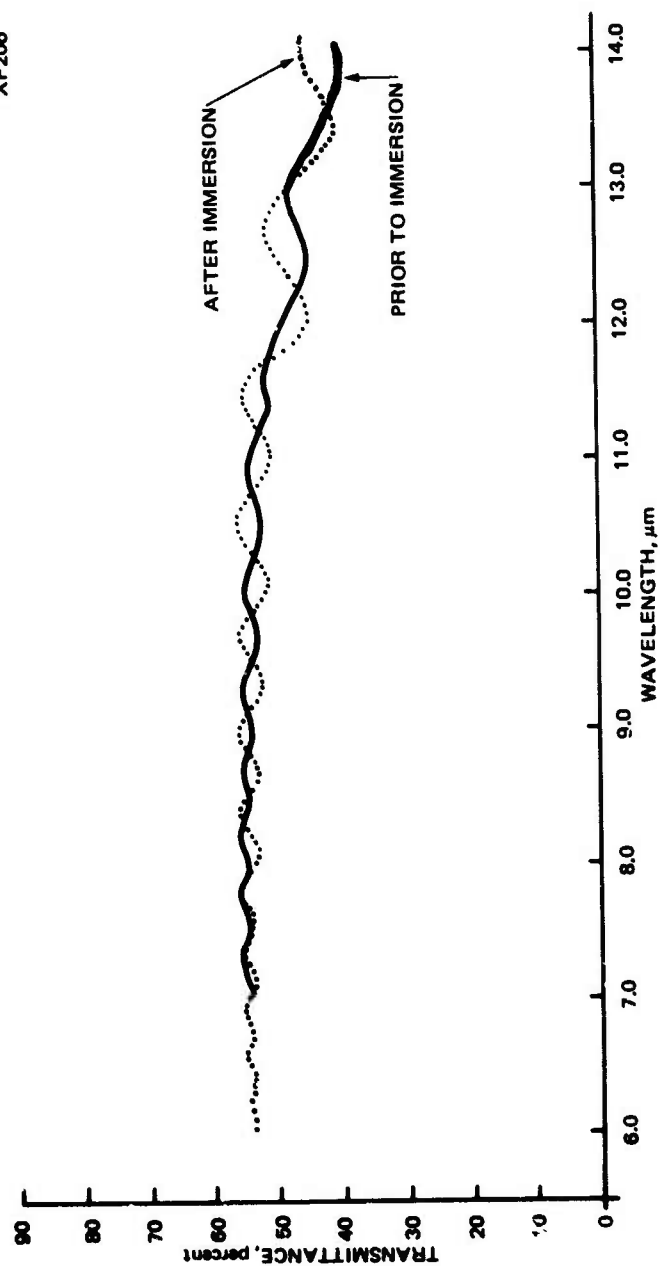
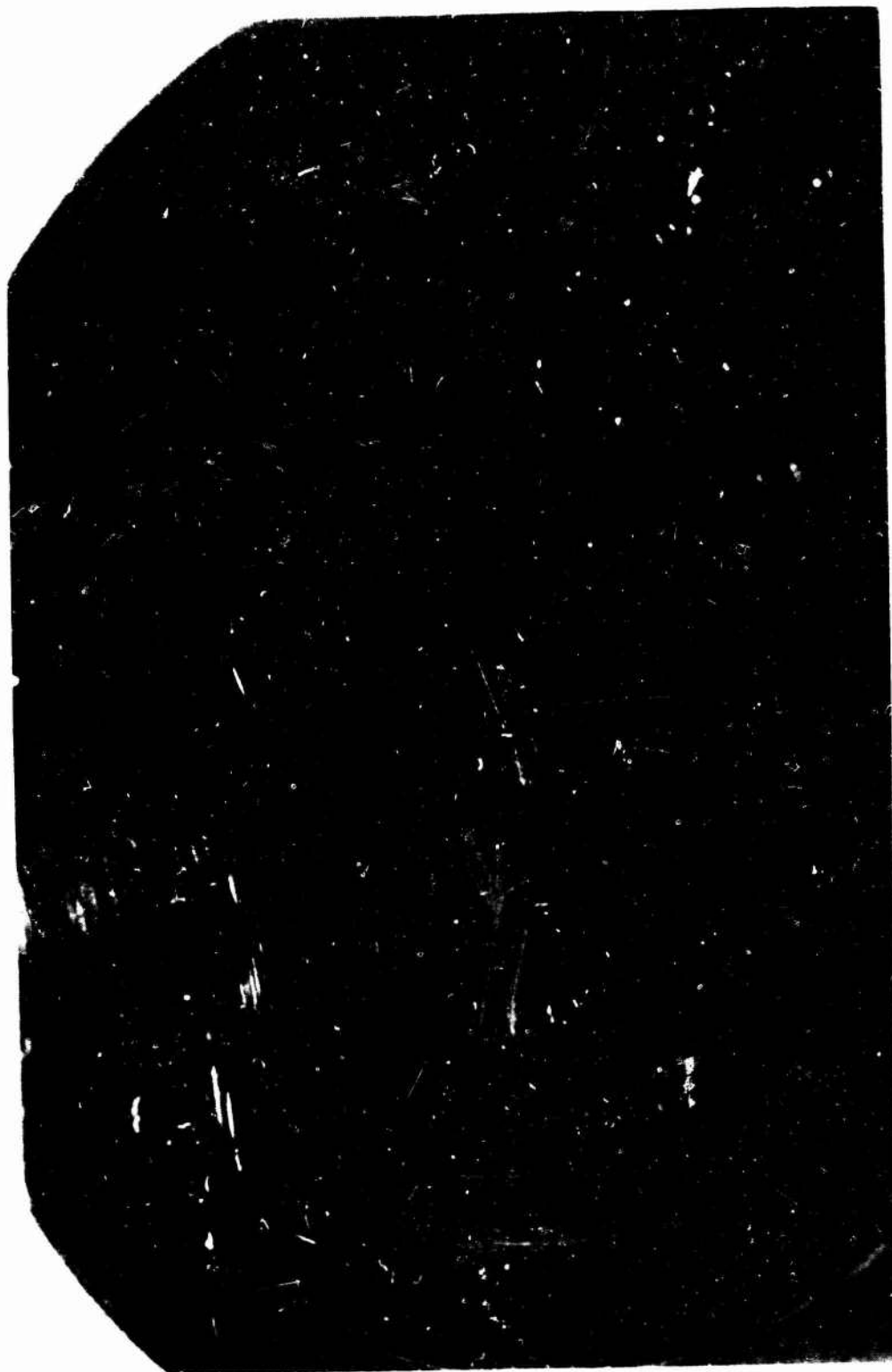


Figure 19. The transmittance of a 0.25-inch-thick germanium specimen with a thick chalcogenide glass coating (Optic Electronic XF206) on the sea face. The transmittance was tested prior to and after 4 months' exposure to seawater in San Diego Bay.





Sample #92

$C_2H_6$ ,  $C_4H_{10}$ , top layer is soft, bottom hard.

Figure 20. A germanium specimen with a multilayer carbon coating (Honeywell L00506) after 4 months' exposure to seawater in San Diego Bay; hard, butane-based carbon layer of 0.5- $\mu m$  thickness overlaid with soft, ethane-based carbon layer of 2- $\mu m$  thickness.

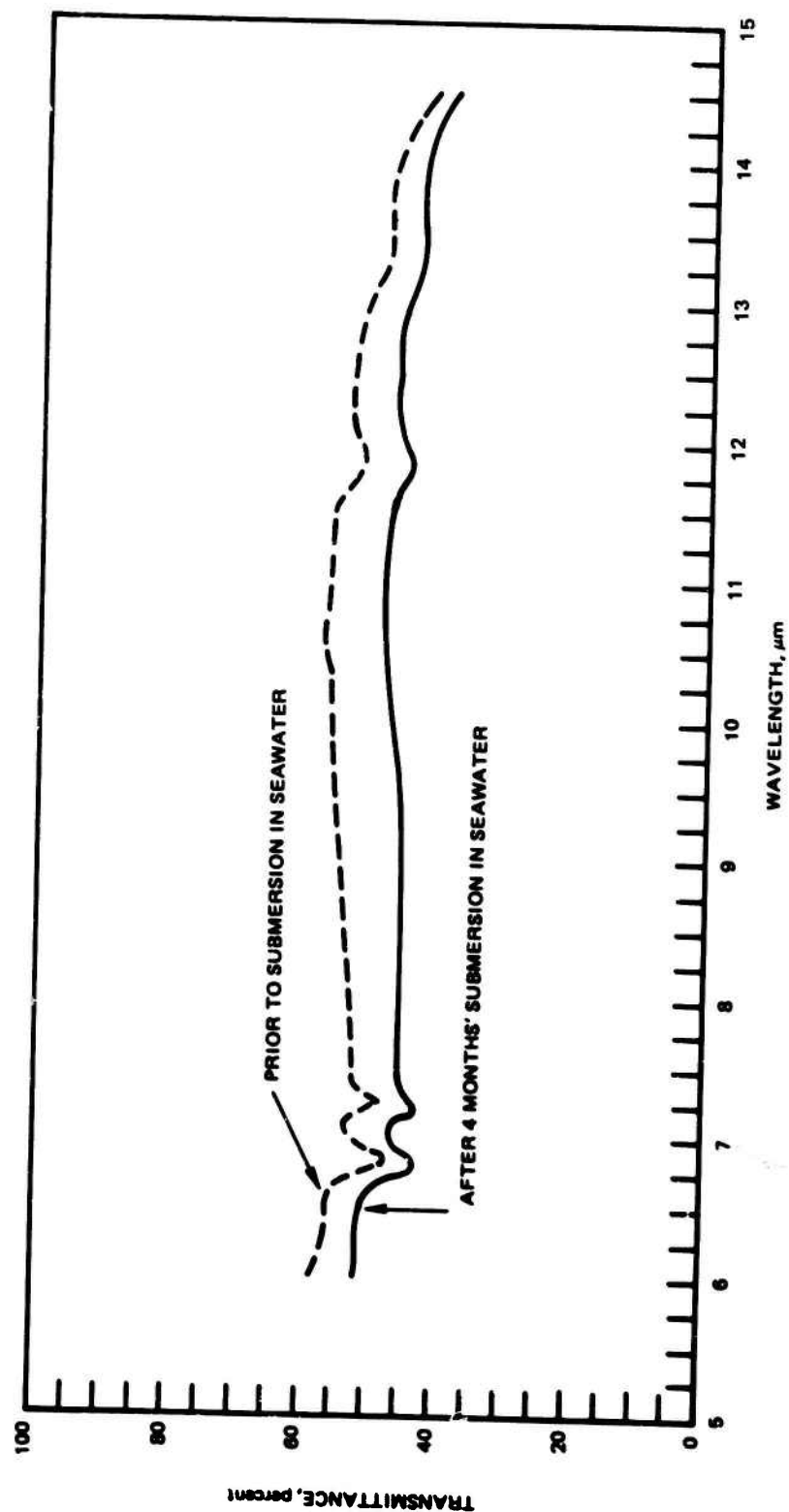


Figure 21. The transmittance of a 0.25-inch-thick germanium specimen with a multilayer carbon coating (Honeywell L00506) on the sea face both prior to and after 4 months' exposure to seawater in San Diego Bay; hard, butane-based carbon layer of 0.5- $\mu\text{m}$  thickness overlaid with soft, ethane-based carbon layer of 2- $\mu\text{m}$  thickness.



9000A, butane, very hard.

Sample #91

Figure 22. A permatium specimen with a monolayer carbon coating (Honeywell V003132) after 4 months' exposure to seawater in San Diego Bay. hard, butane-based carbon layer of 0.9- $\mu$ m thickness.

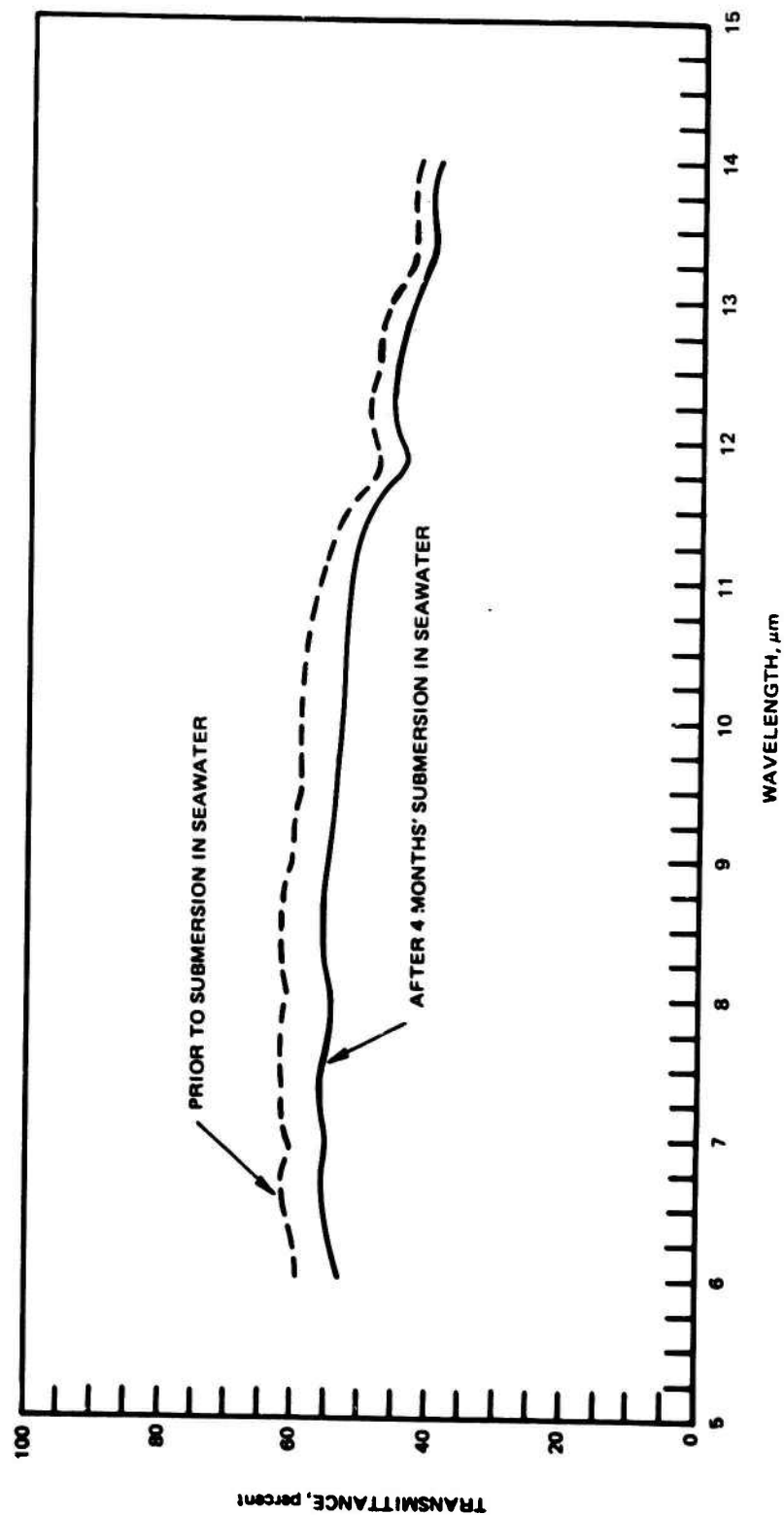


Figure 23. The transmittance of a 0.25-inch-thick germanium specimen with a monolayer carbon coating (Honeywell V003132) on the sea face, both prior to and after 4 months' exposure to seawater in San Diego Bay; hard, butane-based carbon layer of 0.9- $\mu\text{m}$  thickness.



LRO 4719-12-78B

Figure 24. A specimen after 4 months' exposure to seawater with natural current circulation, showing an accumulation of growth.

In phase I of the testing, copper-ion fouling prevention was examined. It has been established that low concentrations of copper ions are toxic to sea life, and that the effective toxicity is a function of the confined water space geometry. Several configurations utilizing copper materials were tested (ref 2) and the results were encouraging. The best results were in configurations in which a relatively static amount of seawater was in contact with the test specimen and the copper-ion source. Note that it is not necessary that the toxic substance concentration be high, nor that the water volume be hermetically confined. By merely altering the geometry about the optical element to restrict water flow, the dwell time of the toxic substance in the vicinity of the optical element is increased and this eliminates a substantial amount of growth from the optical area. It was therefore surmised that similar results as those in the copper ion tests would hold true for antifouling paints, which also leach toxic substances.

In the second phase of testing, further antifouling methods were examined (ref 3). One method involved the addition to the test fixtures of a device to provide forced circulation of seawater. This device consisted of a submersible pump and manifold (fig 4) which would impinge seawater onto the specimens at a rate of 6 ft/s. This method proved effective for localized antifouling protection; however, the sand transported by impinging water had an abrasive effect on the specimen's surfaces and coatings. Specimens whose surfaces were subjected to a steady water flow generally deteriorated more rapidly than specimens not subjected to forced water circulation over the same period of time (fig 10).

Another antifouling method tried in the second phase of testing was the use of electrical current for resistance heating. Resistance heating was first postulated as a method for the prevention of ice formation on germanium windows (ref 6), and it was thought that this method might also have the beneficial effect of discouraging marine growth. The results of the testing were not encouraging (ref 2). When current was applied to specimens submerged in seawater, accelerated corrosion occurred at any minor pinhole in the coating of the specimen. The result was that within a few hours, most of the specimens were corroded, some having major craters (fig 25). In this respect, those specimens with plastic overlays generally fared better than other specimens, but no specimen did exceedingly well under these conditions.

In further phases of testing, the forced seawater circulation and/or fresh water rinsing proved most beneficial in discouraging biofouling. Fresh water rinsing, first used in phase III of the testing, consisted of raising the test fixtures from the ocean two to three times per week and hosing off any accumulated sea life with a spray of tapwater. This proved quite effective as the spray could be directed visually toward any particular concentrations of fouling until the fouling was dislodged; at the same time, spray was not a continuous flow of water containing particulate matter as in the case of the forced circulation of seawater, and hence no coating damage resulted. (Note, however, that this method of fouling prevention might prove operationally impractical for windows mounted on submarines.)

Excessive coating damage was avoided in the fourth phase of testing, in which the forced circulation of seawater was also used for fouling protection, by regulating the pumping mechanism (the same used in phase II) so that water was being pumped only 50 percent of the time. This provided enough circulation to discourage growth, without as much damage to the coatings. The newer, more durable coating also held up better under the constant impinging spray than the original coatings.

This antifouling method was also used in the fifth (and final) phase of testing.



LRO 3673-9-78

Figure 25. A specimen, heated by application of electric current to the germanium while submerged in seawater, after less than 1 day of testing. Two large areas of corrosion are centered around deep craters which began as minor pinholes.



## 6. CONCLUSIONS

The following specimens performed well in the five phases of testing. The extent of their corrosion resistance and their transmittance is noted.

1. Unprotected chalcogenide AMTIR-1 glass surfaces showed excellent resistance to seawater corrosion with no measurable loss in transmittance during 4 months' exposure to seawater. The transmittance of uncoated chalcogenide glass specimens was in the 65-to-70-percent range.

2. The chalcogenide AMTIR-1 glass-coated germanium specimen showed excellent resistance to seawater corrosion. There was no measurable loss in transmittance of this specimen after 4 months' exposure to seawater. Germanium windows coated on the wetted surface with chalcogenide glass and on the dry surface with an AR formula exhibited approximately the same transmittance as chalcogenide glass windows that had a bare wetted surface and the dry surface coated with an appropriate AR formula.

3. Of the antireflective coatings, the multilayer coatings performed better than the single-layer coatings, with the Exotic Materials 40100 multilayer durable AR coating on germanium demonstrating the best corrosion resistance of all AR coatings tested. Specimens with this coating showed no significant drop in transmittance after seawater exposure for 4 months, and exhibited only a few minor pits on the surface in this time period. The transmittance of a germanium specimen coated on both surfaces was in excess of 90 percent.

4. The germanium specimen with a 0.9- $\mu\text{m}$ -thick butane-based carbon coating (Honeywell V003132) was extremely resistant to scratches and minor abrasions. After 4 months' exposure to seawater, the specimen suffered only localized pinpoint pitting with some small craters. The transmittance loss was 6 percent or less over the desired wavelength range. It is projected that specimens with this coating would have a minimal amount of pitting with coating thicknesses of 1  $\mu\text{m}$  or more. With thicknesses of less than 1  $\mu\text{m}$ , the butane-based carbon coating is subject to a proportionately increasing amount of pinholes, possibly a result of the method of application.

5. The germanium specimen with multilayer carbon coating configuration, consisting of a 0.5- $\mu\text{m}$ -thick butane-based coating overlaid by an ethane-based overcoat of 2- $\mu\text{m}$  thickness, exhibited very good resistance to seawater corrosion (Honeywell L00506). The specimen lost approximately 9 percent of its initial transmittance after 4 months' exposure to seawater.

The most effective and practical means of discouraging biofouling are either to incorporate copper-ion sources into the window housing to leach toxic substances into the immediate vicinity and thereby discourage biofouling, or to provide a regulated flow of water onto the surface of the window. An ideal velocity for the impinging water has not yet been established, even though this study has shown that a 6-ft/s velocity definitely prevents biofouling. The selection of the ideal velocity also would have to take into account the resistance of the chosen substrate and/or coating to the impinging water, as excessive velocities tend to abrade the coating prematurely.

## 7. RECOMMENDATIONS

1. Antifouling apparatus such as copper-ion sources or water-jetting mechanisms should be incorporated in the design of the window housings to aid in discouraging biofouling on the windows.



2. Further research should be conducted toward the improvement of one or all of the materials and coatings enumerated below. More extensive testing is necessary to weigh the advantages and disadvantages of each material and coating under different operational scenarios, as follows:

- a. The use of chalcogenide glass ( $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ ) as a primary window material, or as a coating for germanium, should be further researched as both approaches have the potential of significantly extending the service life of IR windows in a marine environment beyond the longest documented life expectancy of any of the multilayer AR coatings. It is preferable, if structurally feasible, to employ chalcogenide glass as the primary window material rather than as a coating for germanium since (1) the service life of a solid-glass window exceeds that of a glass-coated germanium window, (2) the transmittance of chalcogenide glass coated with the standard AR formula on the unwetted surface is higher over a wider range of wavelengths than the transmittance of germanium similarly AR-coated on the dry surface and protected on the wetted surface by a thick chalcogenide glass layer, and (3) the cost of chalcogenide glass is less than that of germanium. The average value of transmittance is in the 70-to-80-percent range.
- b. The durable multilayer, antireflection coating Exotic Materials 40100 is recommended for application on germanium windows that must provide and maintain transmittance of over 90 percent in the 8-to-12- $\mu\text{m}$  range during submersions of up to 6 months. It is postulated that a germanium window coated with Exotic Materials 40100 will survive 6 to 12 months with only minor pitting and less than 10-percent decrease in transmittance.
- c. The use of 1- $\mu\text{m}$  or thicker butane-based hard carbon coating on germanium provides unsurpassed scratch resistance and adequate corrosion resistance with a transmittance loss of approximately 6 percent over a 4-month period of seawater exposure. The initial transmittance of a germanium window protected on the wetted surface with carbon and on the inner surface with standard AR coatings is approximately the same as that of a germanium window coated on both surfaces with durable, multilayer AR coatings; however, the loss in transmittance during long-term submersion is significantly greater than for durable AR coatings. Further research is necessary to determine whether the carbon coatings can be applied with fewer pinholes, since these provide access for seawater to corrode the germanium substrate.

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## APPENDIX

### INTRODUCTION

This appendix contains an overview of procedures and results of the phase V testing which is not separately published elsewhere.

Phase V of the test series introduced a new, hard carbon-type coating produced by Honeywell (ref 8; fig 26). These coatings (table 5) were of varying thicknesses and some contained layers of two types of coatings. Two of the six specimens were coated on both faces; the remaining four were coated on the wetted face only.

### PROCEDURES AND RESULTS

The testing took place at pier 160, NOSC Bayside, with test procedures and equipment as described in the body of this report. The specimens were exposed to seawater for 4 months.

Based on the 4-month testing period, the ethane-based coatings are too soft to be useful alone or with plastic coating overlays. Specimen #96, with 1- $\mu$ m-thick ethane-based coating (D004231), and specimen #95, with polyethylene-covered 1- $\mu$ m-thick ethane-based coating (D004232), suffered severe etching and deterioration during exposure to seawater for 4 months (fig 27 and 28).

The transmittance of specimen #95 dropped from 20 to 30 percent in the 8-to-14- $\mu$ m-wavelength range after exposure to seawater (fig 29). The average transmittance prior to exposure was 45 percent. The transmittance of specimen #96 dropped an average of 25 to 30 percent over the wavelength range (fig 30) during the same period. The transmittance after exposure averaged 30 percent from 8 to 10  $\mu$ m, and sloped down to 8 percent at 14  $\mu$ m.

Conversely, the butane-based coatings were found to be very hard and therefore relatively scratch-resistant. Specimen #91, with the 0.9- $\mu$ m-thick butane-based coating, suffered localized pinpoint pitting and had approximately a dozen small craters after the testing period of 4 months' exposure to seawater (fig 22). The specimen suffered a transmittance loss of only 6 percent or less over the 8-to-14- $\mu$ m wavelength range after exposure to seawater (fig 23), sloping from 55-percent transmittance at 8  $\mu$ m to 40 percent at 14  $\mu$ m.

Specimen #94, with 0.58  $\mu$ m of butane-based (L005094) coating on both sides suffered a greater amount of pinhole pitting and cratering than the 0.9- $\mu$ m coating (fig 31). The specimen appeared to have been initially coated unevenly, and this corresponded to the more extensive patches of cratering. The percent transmittance of the specimen coated with the 0.58- $\mu$ m-thick butane-based coating dropped an average of 10 percent over the 8-to-14- $\mu$ m wavelength range (fig 32). The transmittance after exposure varied in an even curve from 60 percent at 8  $\mu$ m to 46 percent at 14  $\mu$ m.

The two specimens which had a hard butane-based coating overlaid with a layer of the soft ethane coating proved to have the superior carbon coatings. Specimen #92 (L00506) had a 0.5- $\mu$ m-thick lower layer of butane-based coating and a 2- $\mu$ m-thick top layer of ethane-based coating (fig 19). This specimen had the least amount of pitting of any of the hard carbon specimens tested. The specimen suffered less than a dozen pinpoint pits during the 4 months of exposure to seawater. There were some superficial scratches, but these did not penetrate the base coating to reach the substrate. The transmittance of the specimen after

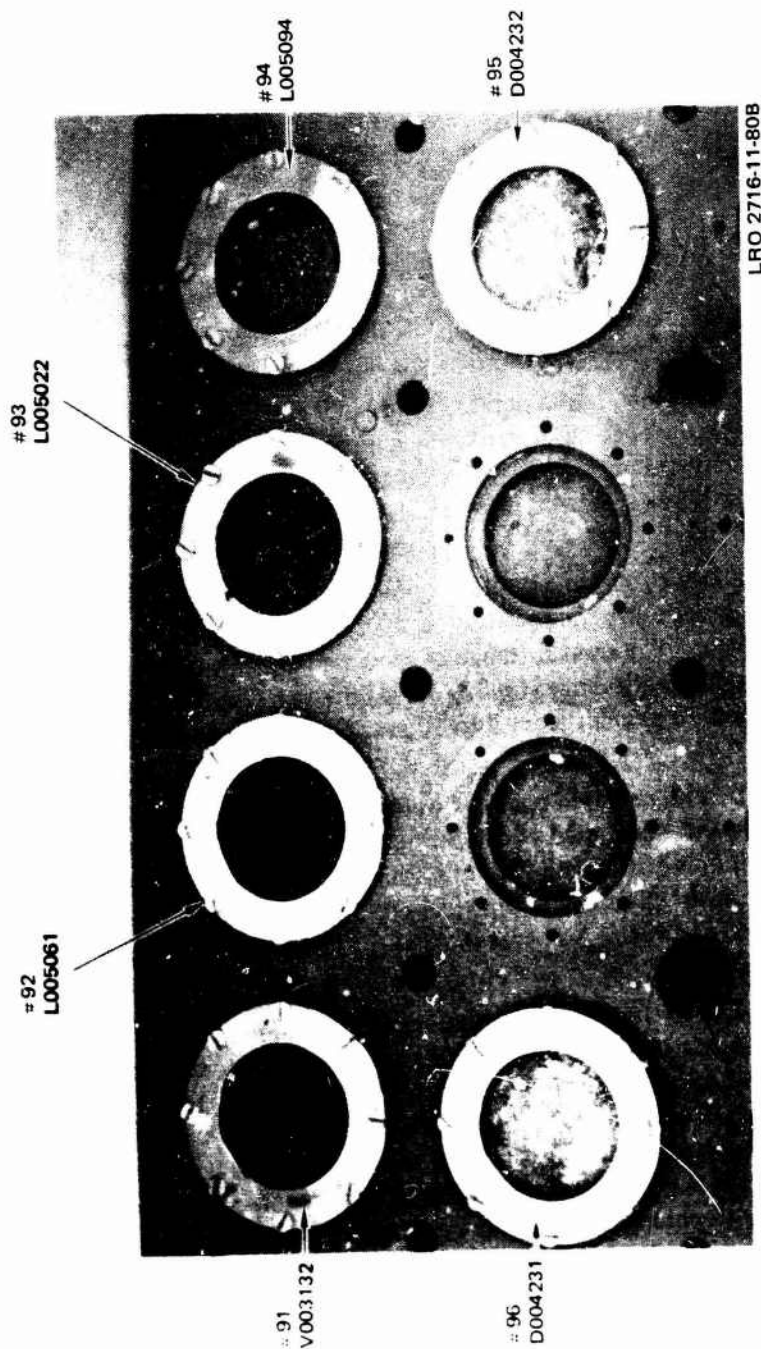
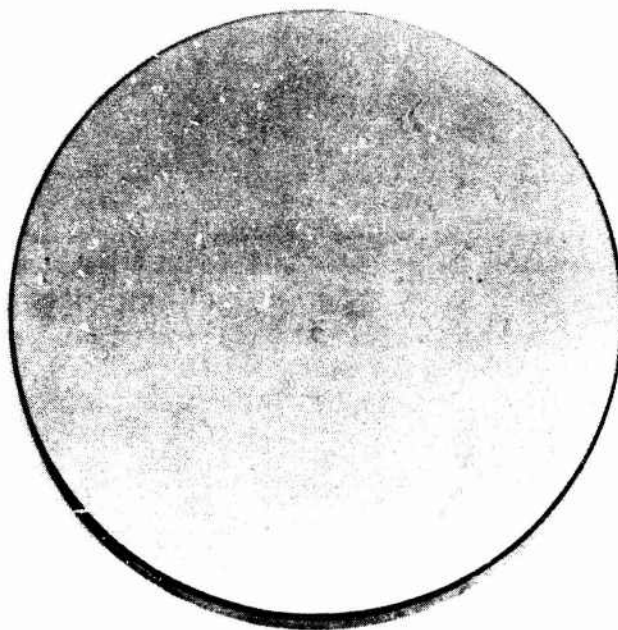


Figure 26. The carbon-coated specimens tested in Phase V, after 4 months' exposure to seawater in San Diego Bay.



(a)

LRO 1838-7-808



(b)

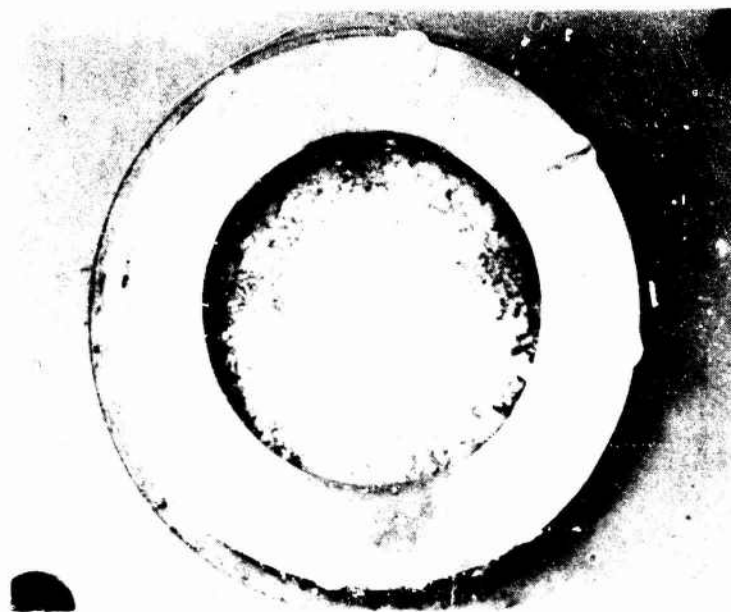
LRO 2722-11-808

Figure 27. A germanium specimen with a  $1\text{-}\mu\text{m}$ -thick ethane-based carbon coating protected by an ethylene layer (Honeywell D004232) both (a) prior to and (b) after 4 months' exposure to seawater in San Diego Bay.



(a)

LRO 1839-7-80B



(b)

LRO 2721-11-80B

Figure 28. A germanium specimen with a 1- $\mu$ m-thick ethane-based carbon coating (Honeywell D004231) both (a) prior to and (b) after 4 months' exposure to seawater in San Diego Bay.

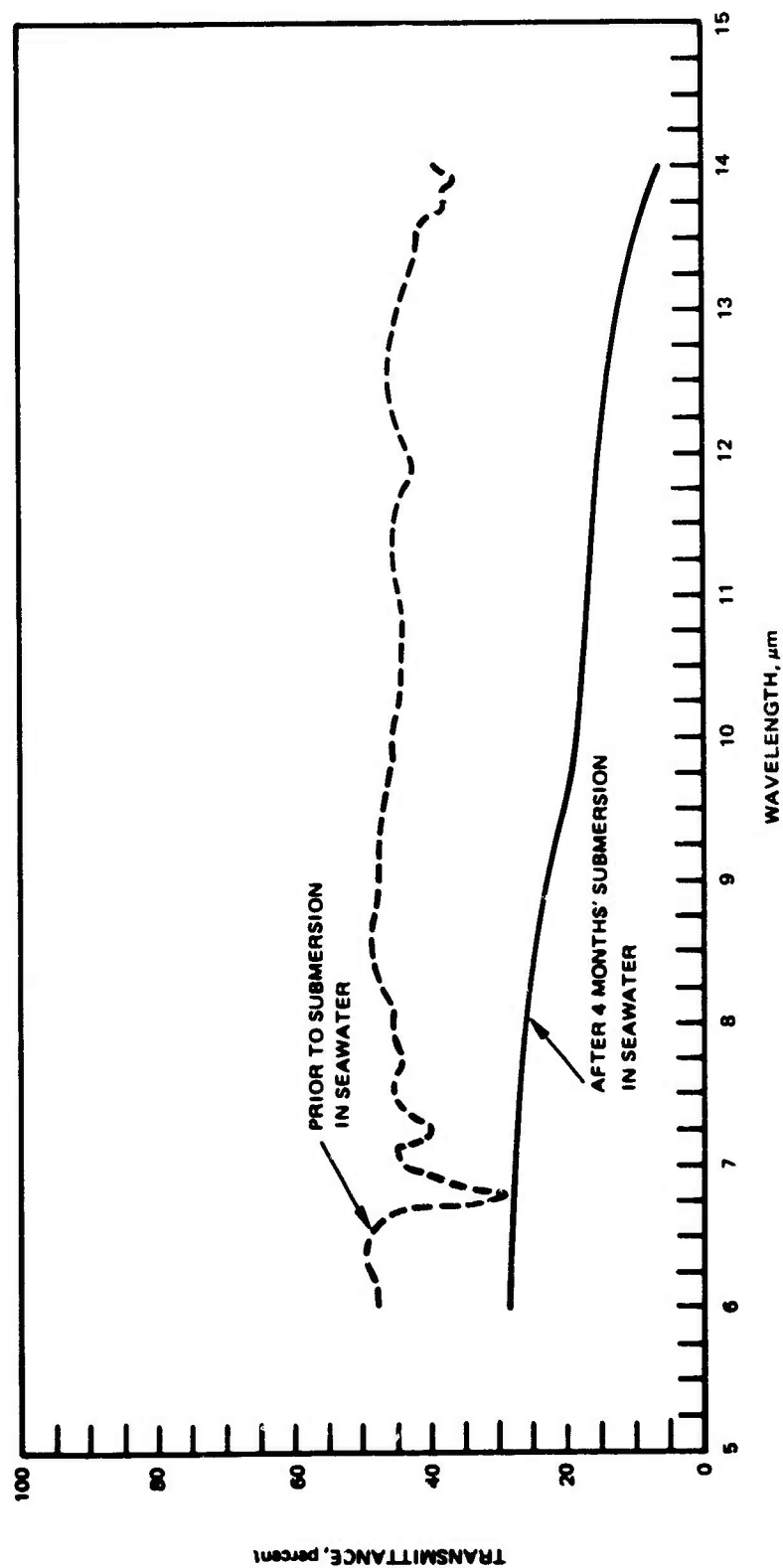


Figure 29. The transmittance of a 0.25-inch-thick germanium specimen with a 1- $\mu\text{m}$ -thick ethane-based carbon coating protected by an ethylene layer (Honeywell D004232) on the sea face, both prior to and after 4 months' exposure to seawater in San Diego Bay.

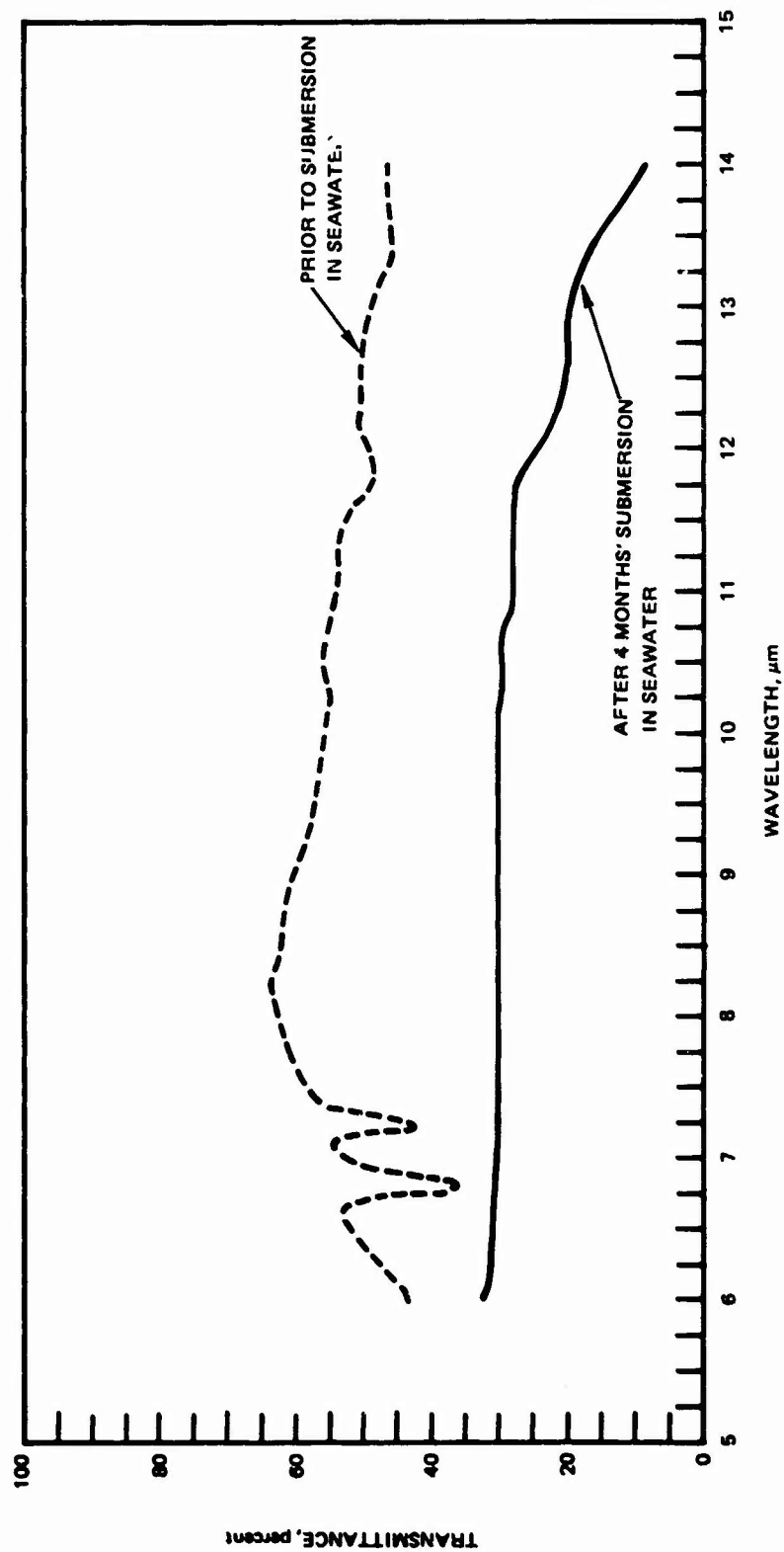


Figure 30. The transmittance of a 0.25-inch-thick germanium specimen with a 1- $\mu\text{m}$ -thick ethane-based carbon coating (Honeywell D004231) on the sea face, both prior to and after 4 months' exposure to seawater in San Diego Bay.





C<sub>4</sub> H<sub>10</sub> 5800A, very hard.

Sample #94

Figure 31. A permatum specimen with a 0.5- $\mu$ m-thick, butane-based coating (Honeywell L005094) after 4 months' exposure to seawater in San Diego Bay.

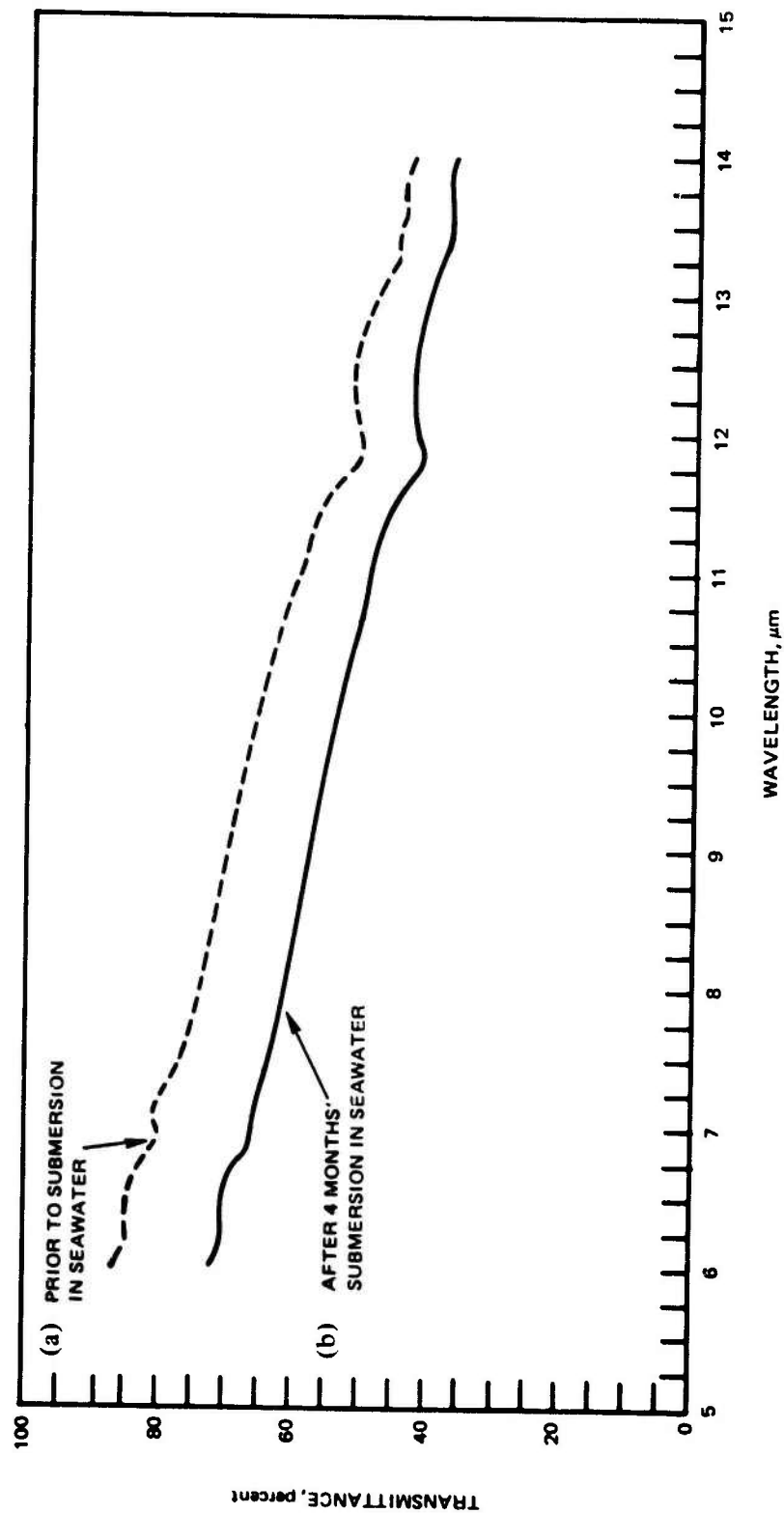


Figure 32. The transmittance of a 0.25-inch-thick germanium specimen with a 0.5- $\mu\text{m}$ -thick butane-based coating (Honeywell L005094) on both faces, both (a) prior to and (b) after 4 months' exposure to seawater in San Diego Bay.

exposure to seawater averaged 45 percent in the 8-to-14- $\mu$ m wavelength range (fig 21), having lost an average of 9 percent of its initial transmittance over the wavelength range.

The #93 (L005022) specimen with the two-layer coating had a 0.5- $\mu$ m-thick butane-based bottom layer and a 1- $\mu$ m-thick ethane-based top layer of coating on both sides. This specimen (fig 32) had a much greater amount of pitting than specimen #92 with the thicker ethane layer. After 4 months' exposure to seawater, the specimen had more than 100 pin-point pits and approximately two dozen small craters. The transmittance prior to submersion sloped downward from 77 percent at 6- $\mu$ m wavelength to 41 percent at 14- $\mu$ m wavelength (fig 33). After the testing period, the transmittance dropped by approximately 10 percent in the lower end of the wavelength spectrum. The drop in transmittance was not as severe in the upper wavelength ranges, losing only 4 percent at 14  $\mu$ m (fig 34).

### CONCLUSIONS

The following statements may be made, based on the findings of this test.

1. An ethane-based carbon coating is inadequate for germanium substrate protection. Even with a polyethylene overcoat, the ethane-based coating is too soft to withstand prolonged seawater exposure and general handling, and is not recommended as the primary coating for germanium substrate.
2. The butane-based coating is very hard and scratch-resistant, but it is subject to pinholes, especially when applied in less than 0.5- $\mu$ m thickness. Thickness in excess of 1  $\mu$ m is necessary to decrease the number of pinholes to an acceptable level.
3. The carbon coating configuration demonstrating the best corrosion protection for germanium substrate is the hard, butane-based coating overlaid with a soft layer of ethane-based coating. The protective layer of the 2- $\mu$ m-thick ethane-based coating virtually eliminates the pinhole problem of the 0.5- $\mu$ m-thick butane-based coating used alone.

### RECOMMENDATIONS

Hard carbon coatings appear to offer excellent corrosion and scratch resistance to germanium windows when applied in the proper thickness. Additional research, however, must be conducted in carbon coating technology to (1) maximize the AR properties of coating in the 8 to 12- $\mu$ m range of wavelengths and (2) minimize the loss of transmittance under sustained submersion.



$C_2H_6/C_4H_{10}$  top layer soft, bottom hard.

Sample #93

Figure 33. A germanium specimen with a 0.5- $\mu$ m-thick butane-based coating overlaid with 1- $\mu$ m-thick ethane coating (Honeywell L005022) after 4 months' exposure to seawater in San Diego Bay.

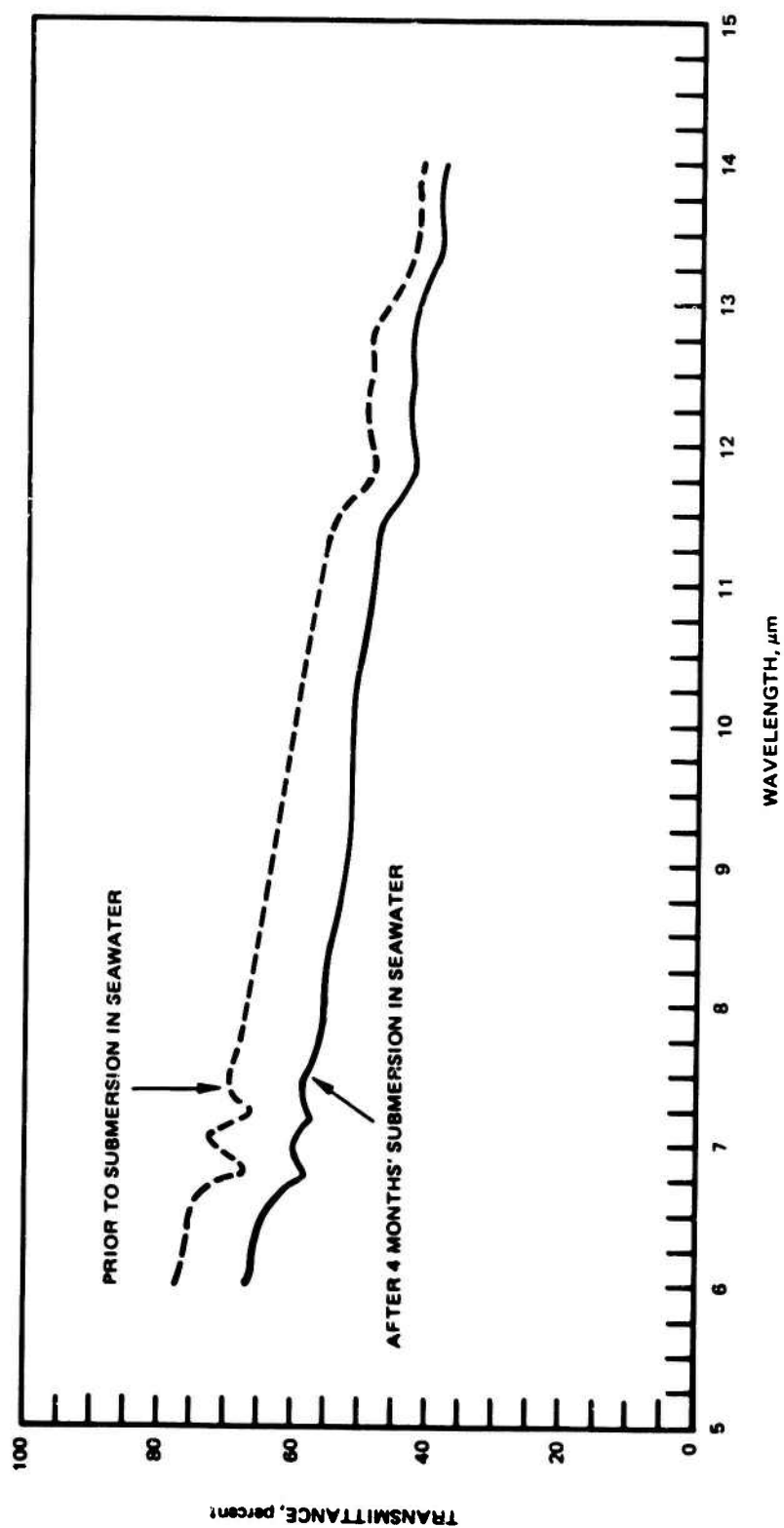


Figure 34. The transmittance of a 0.25-inch-thick germanium specimen with a 0.5-μm-thick butane-based coating overlaid with a 1-μm-thick ethane coating (Honeywell L005022) on both faces, both prior to and after 4 months' exposure to seawater in San Diego Bay.